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High accuracy gravimetric Winkler method for determination of dissolved oxygen

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LIST OF ORIGINAL PUBLICATIONS

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II. L. Jalukse, I. Helm, O. Saks, I. Leito, On the accuracy of micro Winkler titration procedures: a case study, *Accredit. Qual. Assur*. **2008,** 13, 575–579. DOI: 10.1007/s00769-008-0419-1

III. I. Helm, L. Jalukse, M. Vilbaste, I. Leito, Micro-Winkler titration method for dissolved oxygen concentration measurement. *Anal. Chim. Acta*, **2009**, 648, 167–173. DOI:10.1016/j.aca.2009.06.067

IV. I. Helm, L. Jalukse, I. Leito, A new primary method for determination of dissolved oxygen: gravimetric Winkler method. *Analytica Chimica Acta*, **2012**, 741, 21–31. DOI: 10.1016/j.aca.2012.06.049

Author's contribution

Paper I: Main person responsible for planning and writing the manuscript.

Paper II: Performed literature search and wrote large part of the text.

Paper III: Main person responsible for planning and writing the manuscript. Performed all the experimental work.

Paper IV: Main person responsible for planning and writing the manuscript. Performed all the experimental work.

ABBREVATIONS

DO	Dissolved oxygen
FGW	Gravimetric Winkler titration method, where sample preparation is performed in flasks
GUM	The Guide to the Expression of Uncertainty in Measurement
ISO	International Organization for Standardization
PTFE	Polytetrafluoroethene
SGW	Gravimetric Winkler titration method, where sample preparation is performed in syringes
SI	International System of Units
WM	Winkler titration method

1. INTRODUCTION

Dissolved oxygen (DO) content in natural waters is an indispensable quantity whenever background data is collected for investigations of nature from hydrobiological, ecological or environmental protection viewpoint [1]. Sufficient concentration of DO is critical for the survival of most aquatic plants and animals [2] as well as in waste water treatment. DO concentration is a key parameter characterizing natural and wastewaters and for assessing the state of environment in general. Besides dissolved CO_2, DO concentration is an important parameter shaping our climate. It is increasingly evident that the concentration of DO in oceans is decreasing [3–6]. Even small changes in DO content can have serious consequences for many marine organisms, because DO concentration influences the cycling of nitrogen and other redox-sensitive elements [3]. Decrease of DO concentration leads to formation of hypoxic regions (or dead zones) in coastal seas, in sediments, or in the open ocean, which are uninhabitable for most marine organisms [3,7]. DO concentration is related to the changes in the ocean circulation and to the uptake of CO_2 (including anthropogenic) by the ocean [8]. All these changes in turn have relation to the climate change.

Accurate measurements of DO concentration are very important for studying these processes, understanding their role and predicting climate changes. These processes are spread over the entire vast area of the world's oceans and at the same time are slow and need to be monitored over long periods of time. This invokes serious requirements for the measurement methods used to monitor DO. On one hand, the results obtained at different times need to be comparable to each other. This means that the sensors used for such measurements need to be highly stable and reproducible [9]. The performance of oxygen sensors – amperometric and (especially) optical – has dramatically improved in recent years [10].

On the other hand, measurements made in different locations of the oceans have to be comparable to each other. The latter requirement means that the sensors have to be rigorously calibrated so that the results produced with them are traceable to the SI. The sensors need to be calibrated with solutions of accurately known oxygen concentration in order to correct for sensor drift, temperature, salinity and pressure influences [I,11]. Oxygen is an unstable analyte thus significantly complicating sensor calibration.

It has been established that if every care is taken to achieve as accurate as possible results then the accuracy of DO measurements by amperometric sensors is limited by calibration [11] and specifically by the accuracy of the reference DO concentration(s) that can be obtained [I]. This is similar with optical sensors: their lower intrinsic uncertainty may make the relative contribution of calibration reference values even larger [10].

The issues with sensors, among them issues with calibration, have caused a negative perception about the data using sensors in the oceanography commu-

nity and because of this the recent issue of the World Ocean Atlas [12] was compiled with taking into account only DO concentrations obtained with chemical titration methods (first of all the Winkler titration method, WM) and rejecting all sensor-based data. Similar decision was taken in a recent study of DO decline rates in coastal ocean [6]. It is nevertheless clear that there is need for large amounts of data, so that the slow and clumsy titration method cannot satisfy this need. It is necessary to be able to collect data automatically and in large amounts. It is thus expected that eventually sensors will be "back in business". In order to achieve this the accuracy of their calibration needs to be improved.

There are two ways to prepare DO calibration solutions with known concentrations: (1) saturating water with air at fixed temperature and air pressure and using the known saturation concentrations [13–15] and (2) preparing a DO solution and using some primary measurement method for measuring DO concentration. The premier method for the second way is the WM [16] which was first described by Winkler [17] more than hundred years ago. Nowadays the use of WM as the standardizing method is even more important than measurements in the real samples [1]. Also gasometry is an old method for DO determinations, but it is a partly physical method requiring quite specific and complex experimental setup and is therefore not routinely used nowadays.

DO measurement practitioners currently almost exclusively use the saturation method for calibration of DO measurement instruments. This method gives quite accurate results when all assumptions made are correct. DO values obtained with the saturation method are also used in this work for comparison with the WM values. Nevertheless, the saturation method uses ambient air – a highly changing medium – as its reference, thereby relying on the assumption that the oxygen content of the Earth's atmosphere is constant, which is not entirely true [4]. The oxygen content of air depends on air humidity and CO_2 content, which both can change over a wide range of values. Also, this method needs careful accounting for air pressure, humidity and water temperature. It is customary to use published values of DO concentrations in air-saturated water at different temperatures. At the same time, different published values are in disagreement by up to 0.11 mg dm^{-3} at 20 ^{o}C and even up to 0.19 mg dm^{-3} at 40 ^{o}C [15]. Thus the saturation method has many factors that influence the results and it is difficult to realize it in a highly accurate way. An independent primary method, such as WM, would be free from these shortcomings.

The Winkler method is known for a long time, it has been extensively studied and numerous modifications have been proposed [16,18–23]. There have, however, been very few studies using WM that report combined uncertainties taking into account both random and systematic factors influencing the measurement [II]. Usually repeatability and/or reproducibility data are presented that do not enable complete characterization of the accuracy of the methods and tend to leave too optimistic impression of the methods. Very illuminating in this respect are the results of an interlaboratory comparison

study [24] where the between-lab reproducibility standard deviation is as large as 0.37 mg dm^{-3} [24]. In light of this data three original publications [20–22] of so-called micro Winkler procedures (sample volumes 1 to 10 ml instead of 100 to 200 ml for classical Winkler titration) were taken under examination [II] and using the experimental data from those publications uncertainty estimates were calculated by using the Nordtest [25] method. As a result, uncertainty estimates of these three methods were obtained ranging from 0.13 to 0.27 mg dm^{-3} ($k = 2$ expanded uncertainty), which are quite high [II]. These uncertainty estimates reveal that there is a lot of room for improvement of the Winkler method.

Winkler method is the primary method of DO concentration measurement: the obtained mass DO in the sample is traceable to the SI via mass measurement. In this work a realization of the Winkler method with the highest possible accuracy and a careful analysis of the method for its uncertainty sources is presented. First, a very precise and accurate WM for small samples (9–10 ml) is developed. By using this method the uncertainty decreased in the range of 0.08–0.13 mg dm^{-3} ($k = 2$ expanded uncertainty) [III]. Uncertainty analysis was carried out on the basis of ISO GUM [26]. It was comprehensive and gave information about uncertainty sources and their contribution. By analyzing the results of this uncertainty estimation it was seen, that there were still some opportunities for decreasing the uncertainty by modifying the procedure and equipment. As a result of this, the method was further refined and uncertainty in the range of 0.023 to 0.035 mg dm^{-3} (0.27 to 0.38% relative, $k = 2$ expanded uncertainty) was achieved [IV].

This work prepares the ground for putting the DO measurements as such onto a more reliable metrological basis, enabling lower uncertainties and allowing detection of trends and relationships that may remain obscured with the current level of accuracy achievable for DO determination.

2. PRINCIPLE OF THE WINKLER METHOD

The Winkler method is based on quantitative oxidation of Mn^{2+} to Mn^{3+} by oxygen in alkaline medium and on the subsequent quantitative oxidation of iodide to iodine by Mn^{3+} in acidic medium [18,27]. The formed iodine is titrated with thiosulphate.

First, two solutions (Winkler reagents) are added to the oxygen-containing sample: one containing KI and KOH and the other containing $MnSO_4$. Oxygen reacts under alkaline conditions with Mn^{2+} ions forming manganese(III)-hydroxide [18,27]:

$$4Mn^{2+} + O_2 + 8OH^- + 2H_2O \rightarrow 4Mn(OH)_3 \downarrow \quad (1)$$

The solution is then acidified. Under acidic conditions Mn^{3+} ions oxidize iodide to iodine, which eventually forms I_3^- ions with the excess of I^- [18, 27]:

$$2Mn(OH)_3\ (s) + 6H^+ \rightarrow 2Mn^{3+} + 3H_2O \quad (2)$$

$$2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2 \quad (3)$$

$$I_2 + I^- \rightarrow I_3^- \quad (4)$$

The concentration of the formed tri-iodide ions I_3^- (below termed simply as iodine) is usually determined by titration with sodium thiosulphate solution:

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-} \quad (5)$$

Thiosulphate solution is standardized using potassium iodate (KIO_3). Under acidic conditions iodine is formed quantitatively according to the following reaction:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad (6)$$

All the above reactions are fast and proceed quantitatively.

3. EXPERIMENTAL

In this section two developed gravimetric Winkler methods and their mathematical models are described in detail. These methods are called here and below syringe gravimetric Winkler (SGW) [III] and flask gravimetric Winkler (FGW) [IV], respectively. In the first one the sample treatment is carried out in the syringe, in the second one in the flask. As a result of the SGW and its uncertainty analysis it was found, that there is still room for improvements and it is possible to decrease the uncertainty even more. This is done in this work. Photos visualizing the steps of the methods are presented in Appendix 1.

3.1. General notes

In this section also essential uncertainty sources and ways of their estimates of two developed gravimetric Winkler methods are described. Uncertainty estimations for both methods have been carried out according to the ISO GUM modeling approach [26]. If the output quantity Y is dependent on a number of input quantities as follows

$$Y = F(X_1, X_2, \ldots, X_n) \tag{7}$$

then the combined standard uncertainty of the estimate y of the output quantity is found by combining the uncertainty components $\frac{\partial Y}{\partial X_i} u(x_i)$ (termed below also as absolute uncertainty components) of the input quantities X_i according to the following equation [26]:

$$u_C(y) = \sqrt{\left[\frac{\partial Y}{\partial X_1} u(x_1)\right]^2 + \left[\frac{\partial Y}{\partial X_2} u(x_2)\right]^2 + \ldots.. + \left[\frac{\partial Y}{\partial X_n} u(x_n)\right]^2} \tag{8}$$

Technically the uncertainty evaluation was carried out using the Kragten spreadsheet method [36]. The measurands are concentration of DO in the water sample (C_{O2_s}) expressed in mg dm^{-3}. The measurement models are presented in eqs 11–14 and 16–18 for SGW and FGW, respectively. All molecular masses and their uncertainties were found from atomic masses according to ref 37. In all cases where uncertainty estimates are obtained as ±X without additional information on the probability distribution was assumed rectangular distribution (the safest assumption) and converted such uncertainty estimates to the respective standard uncertainties by dividing with square root of 3 [26]. The uncertainty of water density is sufficiently low to be negligible for our purposes.

Both methods' mathematical models use the value of $\Gamma_{m_Y}^{m_X}$. This quantity is calculated by the general equation 9 and are the average (of six or seven parallel determinations for SGW and FGW, respectively, in the equation marked as *n*) ratios of the amounts of X and Y solutions, used in the analysis.

$$\Gamma_{m_Y}^{m_X} = \frac{\sum_i \frac{m_{X\_i}}{m_{Y\_i}}}{n} \tag{9}$$

Such approach is needed (differently from volumetry), because it is impossible to take exactly the same mass of KIO_3 for titration in all parallel titrations. The uncertainties of $\Gamma_{m_Y}^{m_X}$ take into account the repeatability of titrations. Titrations were carried out gravimetrically to lessen the uncertainty caused by volumetric operations [28]. Detailed description of the calculations and the full uncertainty budget can be found in Appendixes 4 and 5 for SGW (in 22.02.2008) and FGW (in 30.01.2012), respectively.

It has been stressed [18,29] that loss of iodine may be an important source of uncertainty in Winkler titration, however, concrete experimental data on the extent of this effect are rare. In the literature more sources of iodine-related errors have been described [30], such as hydrolysis of iodine by formation of oxyacid anions, which are not capable of oxidizing thiosulphate at the pH of the titration and iodine adsorption on glass surfaces. All these effectively lead to the loss of the iodine. At the same time under strongly acidic conditions additional iodine may form via light-induced oxidation of iodide by air oxygen [18,31]:

$$4I^- + 4H^+ + O_2 \rightarrow 2I_2 + 2H_2O \tag{10}$$

This process leads to the increase of iodine concentration. All these factors can have influence both during titration of the sample and during titrant standardization.

In present work iodine volatilization is determined by additional experiments. While titration conditions are different for two gravimetric Winkler methods, then also the volatilized iodine amounts are different. At SGW titration vessel is capped with plastic cap and it makes iodine difficult to vaporize because vapor pressure above the solution is high.

At FGW for the end-point determination an electrode is used and that's why it is not convenient to cap the titration vessel, so that the amount of volatilized iodine is about 16 times higher (it depends highly also on stirring speed). That is why iodine volatilization is differently handled at two gravimetric Winkler methods: at SGW it is accounted only as an uncertainty component, at FGW the amount of volatilized iodine is added or subtracted (depending on where the iodine is coming from) and accounted also as uncertainty sources.

Due to the small sample volume the possible sources of parasitic oxygen have to be determined and their influence minimized. The concentration of oxygen in air per volume unit is more than 30 times higher than in water saturated with air. Therefore avoiding air bubbles is extremely important when taking the samples and when adding the reagent solutions. The two main sources of parasitic oxygen are: DO in Winkler reagent solutions (with possible additional effect from the adding procedure) and sample contamination by the atmospheric oxygen.

3.2. Syringe gravimetric Winkler

All weighings were done on a Mettler Toledo B204-S analytical balance (resolution 0.0001 g). This balance was regularly adjusted using the external adjustment (calibration) weight (E2, 200 g, traceable to the Estonian National mass standard). Uncertainty components of all weighings are: rounding of the digital reading (±0.00005 g, u(rounding)=0.000029 g); linearity of the balance (±0.0002 g, u(linearity)=0.000115 g); drift of the balance (determined in five separate days during 8 hours, relative quantity, u(drift)=0.00024%); and repeatability (determined on two days weighing different weights or their combinations for ten times, calculated as pooled standard deviation, u(repeatability)=0.00016 g). Latter one is used for weighing solid KIO_3 only, the repeatability of weighing during the titrations is accounted for by the Γ factors based on the actual parallel titrations data, see eq 9. Thereat weighing systematic components are considered as factors, which have unity values and uncertainties corresponding to the relative uncertainties of the effects they account for.

All solutions were prepared using distilled water.

3.2.1. Measurement model of the syringe gravimetric Winkler

Potassium iodate (KIO_3) was used as standard titrimetric substance. The stock solution concentration was found according to eq 11

$$C_{KIO_3} = \frac{m_{KIO_3\_s} \cdot P_{KIO_3}}{M_{KIO_3} \cdot V_{flask} \cdot \rho_{KIO3}} \tag{11}$$

where C_{KIO3} [mol kg^{-1}] is the concentration of the KIO_3 solution, m_{KIO3_s} [g] is the mass of the KIO_3, P_{KIO3} [–] is the purity of KIO_3, M_{KIO3} [g mol^{-1}] is molar mass of KIO_3, V_{flask} [dm^3] is the volume of the flask, ρ_{KIO3} [kg dm^{-3}] is the density of 0.0285% KIO_3 solution. KIO_3 solution density was calculated based

on the data on water density from ref 32 and data of KIO_3 solution density from refs 33 and 34.

Concentration of the $Na_2S_2O_3$ titrant was found by titrating iodine liberated from the KIO_3 standard substance in acidic solution of KI. The titrant concentration was found according to eq 12:

$$C_{\mathrm{Na_2S_2O_3}} = 6 \cdot C_{\mathrm{KIO_3}} \cdot \Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3}} \cdot F_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3\_endp}} \cdot F_{I_2} \qquad (12)$$

where C_{Na2S2O3} is the titrant concentration [mol kg^{-1}], m_{KIO3} [g] is the mass of the KIO_3 solution taken for titration, $m_{\mathrm{Na2S2O3\_KIO3}}$ [g] is the mass of the $Na_2S_2O_3$ titrant used for titrating the iodine liberated from KIO_3. $F_{m\mathrm{KIO3}}$ [–] and $F_{m\mathrm{Na2S2O3\_KIO3}}$ [–] are factors taking into account the uncertainties of these solutions weighing. $F_{m\mathrm{KIO3\_endp}}$ [–] is the factor taking into account the uncertainty of determining the titration end-point, F_{I2} [–] is the factor taking into account evaporation of iodine from the solution. These factors have values of unity and uncertainties corresponding to the relative uncertainties of the effects they account for.

The concentration of parasitic DO in the reagents $C_{\mathrm{O2\_reag}}$ [mg kg^{-1}] was found as follows:

$$C_{\mathrm{O_2\_reag}} = \frac{1}{4} \cdot M_{\mathrm{O_2}} \cdot C_{\mathrm{Na_2S_2O_3}} \cdot \Gamma^{m_{\mathrm{Na_2S_2O_3\_reag}}}_{m_{\mathrm{reag}}} \cdot F_{m_{reag}} \cdot F_{m_{Na_2S_2O_3\_reag}} \cdot F_{m_{reag\_endp}} \cdot F_{I_2} - \frac{O_{2\_\mathrm{syringe}}}{m_{\mathrm{reag}}} \qquad (13)$$

where M_{O2} [mg mol^{-1}] is the molar mass of oxygen, $m_{\mathrm{Na2S2O3\_reag}}$ [g] is the amount of titrant consumed for titration, m_{reag} [g] is the overall mass of the solutions of the alkaline KI and $MnSO_4$ and O_{2_syringe} [μg] is the mass of oxygen introduced by the syringe plunger.

$F_{m\mathrm{reag}}$ [–] and $F_{m\mathrm{Na2S2O3\_reag}}$ [–] are factors taking into account the uncertainties of these solutions weighing. $F_{m\mathrm{reag\_endp}}$ [–] is the factor taking into account the uncertainty of determining the titration end-point. These factors have values of unity and uncertainties corresponding to the relative uncertainties of the effects they account for.

The DO concentration in the sample was found according to eq 14:

$$C_{\mathrm{O_2\_s}} = \rho \cdot \left(\frac{1}{4} \cdot M_{\mathrm{O_2}} \cdot C_{\mathrm{Na_2S_2O_3}} \cdot \Gamma^{m_{\mathrm{Na_2S_2O_3\_s}}}_{m_{\mathrm{s}}} \cdot F_{m_s} \cdot F_{m_{Na_2S_2O_3\_s}} \cdot F_{m_{s\_endp}} \cdot F_{I_2} - C_{\mathrm{O_2\_reag}} \cdot \Gamma^{m_{\mathrm{reag\_s}}}_{m_{\mathrm{s}}} - \frac{O_{2\_\mathrm{syringe}}}{m_{\mathrm{s}}} \right) \qquad (14)$$

where $C_{\mathrm{O2\_s}}$ [mg dm^{-3}] is the DO concentration in the sample, ρ [kg dm^{-3}] is the density of water saturated with air, found according to ref 35, $m_{\mathrm{Na2S2O3\_s}}$ [g] is the mass of $Na_2S_2O_3$ solution consumed for sample titration, m_{s} [g] is the sample mass, $m_{\mathrm{reag\_s}}$ [g] is the overall mass of the added reagent solutions.

F_{m_s} [–] and $F_{m\mathrm{Na2S2O3\_s}}$ [–] are factors taking into account the uncertainties of these solutions weighing. $F_{m\_s\_endp}$ [–] is the factor taking into account the uncertainty of determining the titration end-point. These factors have unity values and uncertainties corresponding to the relative uncertainties of the effects they account for.

3.2.2. Preparing of working solution of KIO_3

Potassium iodate solution with concentration of ca 0.0013 mol kg^{-1} was prepared from 0.28 g (known with the accuracy of 0.0001 g) of KIO_3 in a 1000 cm^3 volumetric flask. Uncertainty components of the 1 dm^3 volumetric flask volume are: uncertainty of the nominal volume as specified by the manufacturer (no calibration was done at our laboratory): $\pm$ 0.4 cm^3 (u(cal)=0.23 cm^3); uncertainty due to the imprecision of filling of the flask: ± 10 drops or ± 0.3 cm^3, u(filling)=0.17 cm^3; uncertainty due to the temperature effect on solution density: u(temperature)=0.24 cm^3. The standard uncertainty of the KIO_3 solution volume was found as $u(V_{\mathrm{flask}})$=0.38 cm^3.

The minimum purity of the KIO_3 was given 99.7 %, so it was assumed that actual purity is 99.85 with the rectangular distribution (the safest assumption) and $\pm$ 0.15% as the uncertainty, giving the relative standard uncertainty as 0.00087.

3.2.3. Determination of the concentration of the $Na_2S_2O_3$ titrant

Iodine solution was prepared as follows. 2 cm^3 of the standard KIO_3 solution (0.0013 mol kg^{-1}) was transferred using a plastic syringe through plastic septum into a dried and weighed titration vessel. The vessel was weighed again. Using another syringe 0.1 cm^3 of solution containing KI (2.1 mol dm^{-3}) and KOH (8.7 mol dm^{-3}) (alkaline KI solution) was added. Using a third syringe ca 0.1 cm^3 of H_2SO_4 solution (5.3 mol dm^{-3}) was added carefully, until the color of the solution did not change anymore. Under acidic conditions iodine is formed according to the reaction 6. The care in adding H_2SO_4 solution is necessary in order to avoid over-acidification of the solution because under strongly acidic conditions additional iodine may form via oxidation of iodide by air oxygen (see the reaction 10). The iodine formed from KIO_3 was titrated immediately (to avoid loss of iodine by evaporation) with ca 0.0025 mol dm^{-3} $Na_2S_2O_3$ solution (reaction 5). Titration was carried out using a glass syringe filled with titrant and weighed. After titration the syringe was weighed again to determine the consumed titrant mass. Six parallel measurements were carried out according to the described procedure and the average result was used as the titrant concentration. Repeatability of the titration and repeatabilities of the masses are

taken into account by the standard deviation of the mean ratio $\Gamma_{\frac{m_{KIO_3}}{m_{Na_2S_2O_3\_KIO_3}}}$ (according to eq 9). Possible systematic effects on the titration end-point are taken into account by the factor $F_{m\mathrm{KIO3\_endp}}$ (see eq 12). The end-point was determined using a visual starch indicator. The uncertainty of end-point determination was estimated as ± 1 drop. Mass of one drop with the used needle was 0.017 g and thus the standard uncertainty was u = 0.01 g.

3.2.4. Sample preparation

Samples were prepared in 10 cm^3 glass syringes with PTFE plungers (Hamilton 1010LT 10.0 cm^3 Syringe, Luer Tip). Masses of all syringes were determined beforehand.

Six parallel samples were taken as follows:

a) The syringe and the needle were rinsed with sample solution.
b) Air bubbles were eliminated by gently tapping the syringe. DO concentration decreases when doing this, therefore the syringe was emptied again so that only its dead volume was filled.
c) The syringe was rinsed again avoiding air bubbles.
d) 9.4 cm^3 of the sample was aspirated into the syringe.
e) The tip of the needle was poked into a rubber septum.

When six syringes were filled with samples and weighed the reagents were added. Ca 0.2 cm^3 of the alkaline KI solution and ca 0.2 cm^3 of $MnSO_4$ solution (2.1 mol dm^{-3}) was aspirated into each syringe. The needle tip was again sealed, the sample was intensely mixed and the $Mn(OH)_3$ precipitate was let to form during 45±10 minutes (according to eq 1). The syringe was weighed again to determine the net amount of the added reagents. This is necessary because the reagents also contain DO, which is taken into account. After 45 minutes ca 0.2 cm^3 of H_2SO_4 solution was aspirated into the syringe. Tri-iodide complex is formed according to reactions 2, 3 and 4. At this stage the air bubbles do not interfere anymore.

3.2.5. Titration of the sample with the $Na_2S_2O_3$ titrant

The formed iodine solution is transferred through a plastic cap to the titration vessel. Simultaneously titrant is added from a pre-weighed glass syringe (to avoid possible evaporation of iodine). The sample syringe was rinsed twice with distilled water and the rinsing water was added to the titration vessel. The solution was titrated with $Na_2S_2O_3$ using a syringe until the solution was pale yellow. Then ca 0.2 cm^3 of 1% starch solution was added and titration was continued until the formed blue color disappeared. The titration syringe was weighed again. The amount of the consumed titrant was determined from mass

difference. Six parallel titrations were carried out. Repeatability of the titration and repeatabilities of the masses were taken into account by the standard uncertainty of the mean ratio $\Gamma^{m_s}_{m_{Na2S2O3\_s}}$ (according to eq 9). Possible systematic effect in finding titration end-point is taken into account by $F_{m\_s\_endp}$ (see eq 14). This uncertainty has been estimated as ± 1 drop. Mass of one drop is 0.017 g leading to the standard uncertainty of 0.01 g.

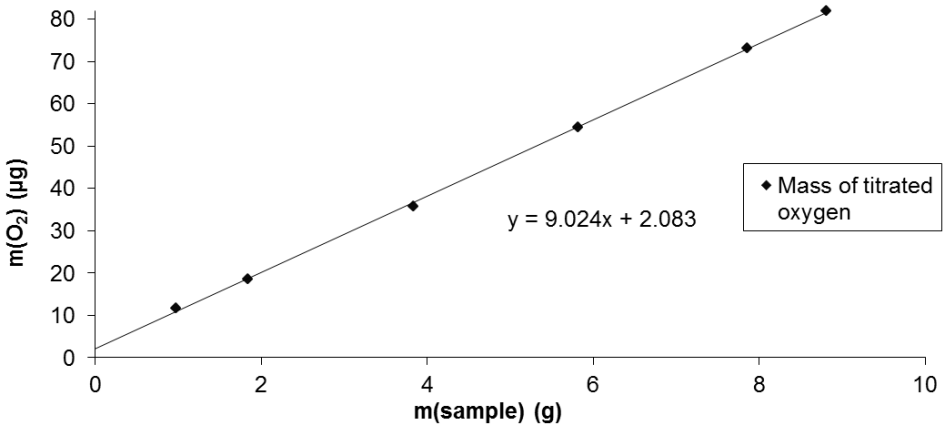
3.2.6. Determination of parasitic oxygen

The overall amount of oxygen introduced by the $MnSO_4$ and the alkaline KI solutions was determined daily by aspirating into the glass syringe ca 2 cm^3 of the solution of KI and KOH, ca 2 cm^3 of $MnSO_4$ and after 45 minutes 2 cm^3 of H_2SO_4 solution was aspirated. The titration was carried out as described above. Repeatability of the titration and repeatabilities of the masses were taken into account by the standard deviation of the mean ratio $\Gamma^{m_{reag}}_{m_{Na2S2O3\_reag}}$ (according to eq 9). Possible systematic effect in finding titration end-point has been estimated as ± 2 drops of titrant. Mass of one drop is 0.017 g leading to the standard uncertainty of 0.02 g.

All polymeric materials can dissolve oxygen. In this work the oxygen dissolved in the PTFE plunger is important. If there is no diffusion of oxygen inside the sample the oxygen concentration should decrease to zero if the sample mass is decreased to zero. If some oxygen diffuses into the sample from the environment (not from the sample itself), then the value of the intercept of the graph equals the amount of parasitic oxygen (axes: amount of oxygen – y-axis, sample mass – x-axis). In order to determine the amount of oxygen introduced from the plunger the DO amount in different quantities of the same sample was determined. The mass of DO found in the sample was plotted against the sample mass. The mass of the parasitic oxygen introduced from the plunger was found as the intercept of the graph (see Graph 1). From the measurement results it can be concluded that some oxygen diffuses into the sample from the PTFE plunger and possibly from the narrow space between the plunger and the syringe barrel. The air-saturated distilled water at 20 °C was used in this experiment and the samples were allowed to precipitate for 45±10 minutes.

The mass of the parasitic oxygen introduced from the plunger was found as the intercept of the graph. The measurements were carried out on six different days and the following results were obtained: 2.69; 1.62; 3.00; 1.23; 2.03; 2.08 µg.

The amount of parasitic oxygen introduced from the plunger was found as 2.11 µg ($O_{2\_syringe}$) with standard uncertainty of 0.27 µg ($u(O_{2\_syringe})$). The $Mn(OH)_3$ precipitate was let to form during 45±10 minutes in this experiment.

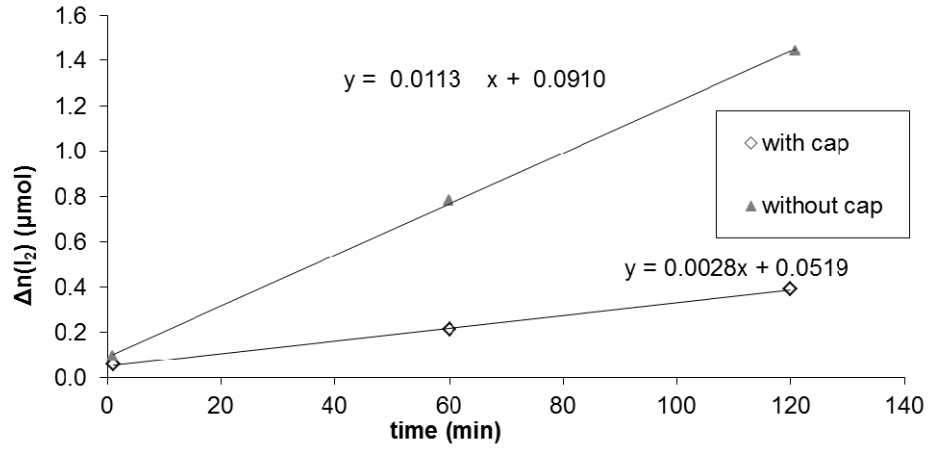


Graph 1. Determination of parasitic oxygen $O_{2\_syringe}$.

3.2.7. Determination of iodine volatilization

An additional experiment was carried out to determine the iodine volatilization amount. The experimental conditions were the same as when standardizing the titrant. Averaged quantity of iodine moles was 7.8 µmol. The measurements were carried out in parallel in two ways: if the titration vessels were covered with plastic caps and if the vessels were open.

Altogether six iodine solutions were prepared – three of them were capped in waiting period and three of them were open. The time gaps used were one minute, two hours and three hours. See the Graph 2.



Graph 2. Determination of iodine volatilization.

The slope of the graph equals the number of volatilized iodine moles in one minute. The results showed that the amount of iodine volatilized in one minute are 0.0028 μmol and 0.011 μmol if capped titration vessel and open vessel were used, respectively. It makes 0.04% and 0.14% of the whole iodine amount (7.78 μmol), respectively. The titration of iodine solution takes time approximately one minute. The uncertainty of iodine volatilization expressed according to eq 15:

$$u(F_{I_2}) = \frac{0.0028\mu mol}{\sqrt{3} \cdot 7.78\mu mol} = 0.00021 \tag{15}$$

In the case of determination of DO in reagents and sample the concentration of iodine solution was lower. Nevertheless it was assumed the same relative volatilization of iodine. So this uncertainty component may be overestimated to some extent.

3.3. Flask gravimetric Winkler

All solutions where accurate concentration was important were prepared by weighing. The amounts of the solutions were measured by weighing. In case of transfers where it was necessary to avoid contact with air oxygen glass syringes with tight plungers and cemented needles were used. In other cases plastic syringes were used.

All amounts of reagents, which directly influenced the result, were measured by weighing. Weighing was done on a Precisa XR205SM-DR balance. The balance was regularly adjusted using the internal adjustment (calibration) weight. This adjustment was additionally checked using 5 independent reference weights in 9 different combinations resulting in masses ranging from 0.01 g to 200 g (and traceable to the SI via the Estonian National mass standard). The obtained differences of the readings from the masses of the weights were too small to justify correction, however they were taken into account in evaluation of mass measurement uncertainty. The balance has two measurement ranges: low: 0–92 g and high: 92–205 g with 4 and 5 decimal places, respectively. So, some of the components of weighing uncertainties have two different values – for higher and for lower range. Which one is used depends on the mass of the object together with tare. The uncertainty components of weighing are: repeatability, rounding of the digital reading, drift of the balance and calibration of the balance. The repeatability uncertainty components for the two ranges were determined as u(repeatability_low)=0.000043 g and u(repeatability_high)=0.000057 g. These estimates are used for weighing of KIO_3 and its solutions. The repeatability of weighing during titration is accounted for by the Γ factors based on the actual parallel titrations data as detailed in section 3.1, see eq 9 there. Rounding of the digital reading is taken

into account in the conventional way, as half of the last digit of the reading assuming rectangular distribution leading to standard uncertainty estimates u(rounding_low)=0.0000029 g and u(rounding_high)=0.000029 g. To estimate the drift of balance three weights (m_1 = 50 g, m_2 = 100 g and m_3 = 100 g) were weighed daily before and after making the Winkler titration. This experiment was carried out on 17 different days. The instrument was adjusted (internal calibration) on every morning before the start of the measurements. The drift of the balance was found to be proportional to the mass and was quantified as u(drift)=0.000064 %. Additional experiment has been done by weighing reference weights. The biggest difference between mass of the reference weight and reading of the used scale was 0.0003 g and it was divided with the mass it was attained (120 g) to get a relative quantity and divided by the square root of three. This gave uncertainty of the calibration of the balance, u(calibration)=0.000042 %.

Two additional uncertainty sources related to weighing were taken into account: possible partial evaporation of water from the KIO_3 solution (u = 0.002 g) and the "warm hand" effect when weighing the titrant syringe after titration (u = 0.00046 g). The latter leads to lower mass of the syringe because it has been warmed by hand during titration and this causes ascending air flow in the balance compartment.

The water used for all operations was produced with a Millipore Milli-Q Advantage A10 setup (resistivity 18.2 MΩ cm). The reagents used were of the highest purity available.

3.3.1. Measurement model of flask gravimetric Winkler

Potassium iodate (KIO_3) was used as the standard substance. The working solution concentration was found according to eq 16.

$$C_{KIO_3III} = \frac{m_{KIO_3\_s} \cdot 1000 \cdot 1000 \cdot m_{KIO_3\_I\_transf} \cdot m_{KIO_3\_II\_transf} \cdot P_{KIO_3}}{M_{KIO_3} \cdot m_{KIO_3\_I} \cdot m_{KIO_3\_II} \cdot m_{KIO_3\_III}} \tag{16}$$

where C_{KIO3_III} [mol kg^{-1}] is the concentration of the KIO_3 working solution, m_{KIO3_s} [g] is the mass of the solid KIO_3, P_{KIO3} [–] is the purity (mass fraction) of KIO_3, M_{KIO3} [mg mol^{-1}] is molar mass of KIO_3, m_{KIO3_I} [g], m_{KIO3_II} [g] and m_{KIO3_III} [g] are the masses of the prepared solutions, respectively, $m_{KIO3\_I\_transf}$ [g] and $m_{KIO3\_II\_transf}$ [g] are the masses of the transferred solutions for diluting the previous solution.

Concentration of the $Na_2S_2O_3$ titrant was found by titrating iodine liberated from the KIO_3 standard substance in acidic solution of KI. The titrant concentration was found according to eq 17.

$$C_{\mathrm{Na_2S_2O_3}} = 6 \cdot C_{\mathrm{KIO_3}} \cdot \Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3}} \cdot F_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3\_endp}} - \frac{2 \cdot n_{I_2\_vol\_t}}{m_{Na_2S_2O_3\_KIO_3}} \quad (17)$$

where C_{Na2S2O3} is the titrant concentration [mol kg^{-1}], m_{KIO3} [g] is the mass of the KIO_3 working solution taken for titration, $m_{\mathrm{Na2S2O3\_KIO3}}$ [g] is the mass of the $Na_2S_2O_3$ titrant used for titrating the iodine liberated from KIO_3, $n_{\mathrm{I2\_vol\_t}}$ [mmol] evaporated iodine from the solution during the titration for determination of titrant concentration. In order to account for the remaining uncertainty sources three factors F are introduced. $F_{m\mathrm{KIO3}}$ [–] and $F_{m\mathrm{Na2S2O3\_KIO3}}$ [–] are factors taking into account the uncertainties of weighing of these solutions. $F_{m\mathrm{KIO3\_endp}}$ [–] is the factor taking into account the uncertainty of determining the titration end-point. These factors have unity values and their uncertainties correspond to the respective relative uncertainty contributions to $\Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}}$.

The DO concentration in the sample was found according to eq 18:

$$C_{\mathrm{O_2\_s}} = \rho \cdot \left(M_{\mathrm{O_2}} \cdot \frac{1}{4} \cdot \left(C_{\mathrm{Na_2S_2O_3}} \cdot \Gamma^{m_{\mathrm{Na2S2O3\_s}}}_{m_s} \cdot F_{m_s} \cdot F_{m_{Na_2S_2O_3\_s}} \cdot F_{m_{s\_endp}} + \frac{2 \cdot n_{I_2\_vol\_s}}{\overline{m_s}} \right) - Int_{O_2} - CF_{\mathrm{O_2}} \cdot \frac{p}{p_n} \right) \quad (18)$$

where $C_{\mathrm{O2\_s}}$ [mg dm^{-3}] is the DO mass concentration in the sample, ρ [kg dm^{-3}] is the density of water saturated with air, calculated according to ref 35. $\Gamma^{m_{Na_2S_2O_3\_s}}_{m_s}$ is the average (from seven parallel determinations) ratio of the masses of $Na_2S_2O_3$ and sample solutions, used in the analysis and is defined analogously to eq 9. The uncertainty of $\Gamma^{m_{Na_2S_2O_3\_s}}_{m_s}$ takes into account only the repeatability of titration, $n_{\mathrm{I2\_vol\_s}}$ [mmol] is the estimated amount evaporated iodine from the solution during the transfer from sample flask to the titration vessel and during the titration, $\overline{m_s}$ is the average mass of the sample. In order to account for the remaining uncertainty sources three factors F are introduced. F_{m_s} [–] and $F_{m\mathrm{Na2S2O3\_s}}$ [–] are factors taking into account the uncertainties of weighing of these solutions weighing. F_{m_endp} [–] is the factor taking into account the uncertainty of determining the titration end-point. These factors have unity values and uncertainties corresponding to the relative uncertainties of the effects they account for. Int_{O2} [mg kg^{-1}] is the input quantity taking into account the contamination of the sample by the parasitic oxygen introduced through the junction between the stopper and the flask neck. CF_{O2} [mg kg^{-1}] is the correction accounting for the parasitic oxygen introduced with reagent solutions. Both these effects lead to apparent increase of DO concentration in the sample (therefore the negative signs of the corrections). CF_{O2} is normalized to the sea-level pressure by multiplying it with the ratio of pressures p [Pa] and p_n [Pa], which are air pressures in the measurement location at the time of the measuring and the normal sea-level pressure, respectively.

3.3.2. Preparing of standard working solutions of KIO_3

Standard solutions were prepared gravimetrically using the highest purity standard substance KIO_3 available (declared purity: 99.997% on metals basis, Sigma-Aldrich). This purity was considered as too optimistic and it was used the following purity estimate: 100.0% ± 0.1%. The true content of KIO_3 in the substance was assumed to be rectangularly distributed in the range of 99.9% to 100.1%, leading to the standard uncertainty of purity 0.058%. KIO_3 is known for its negligible hygroscopicity [31]. This was additionally tested by drying the substance at 110 °C for 4 hours. A mass decrease was not detected.

The working solution was made by consecutive dilutions. The first solution (KIO_3_I, c=36 g kg^{-1}) was made by weighing about 1.4 grams of solid KIO_3 and dissolving it in about 40 grams of water. The second solution (KIO_3_II, c=3 g kg^{-1}) was made by weighing about 3 grams of solution KIO_3_I and adding water to bring the volume to approximately 40 grams. The working solution (KIO_3_III, c=0.2 g kg^{-1} or 1 mmol kg^{-1}) was made by weighing about 4–6 grams of KIO_3_II and adding water to bring the volume up to approximately 100 grams. All these solutions were made into tightly capped bottles to avoid change of concentration of the solutions during and between the analyses.

3.3.3. Determination of the concentration of the $Na_2S_2O_3$ titrant

Concentration of the titrant was determined by titrating a solution of iodine with known concentration. The iodine solution was prepared as follows. About 5 cm^3 of the standard KIO_3_III working solution (0.7 mmol kg^{-1}, see the previous paragraph) was transferred using a plastic syringe into a dried and weighed cylindrical wide-mouth 40 ml titration vessel. The vessel was weighed again. Using two 1 ml syringes approximately 0.2 cm^3 of solution containing KI (puriss. 99.5%, Sigma-Aldrich, 2.1 mol dm^{-3}) and KOH (8.7 mol dm^{-3}) (alkaline KI solution) was added. Using a third syringe approximately 0.2 cm^3 of H_2SO_4 solution (5.3 mol dm^{-3}) was added. Under acidic conditions iodine is formed quantitatively according to the reaction 6. The iodine formed from KIO_3 was titrated with ca 0.0015 mol kg^{-1} $Na_2S_2O_3$ titrant (see reaction 5) as soon as the iodine was formed. It is not possible to use pre-titration here in order to minimize iodine evaporation: until iodate (oxidizing agent) is in the solution sodium thiosulphate (reducing agent) can not be added or else they react each other with a different stoichiometry. Titrations were done using a plastic syringe (20 cm^3, Brown, needle external diameter 0.63 mm) filled with titrant and weighed. The titration end-point was determined amperometrically. Voltage of 100 mV was applied between two platinum electrodes (Metrohm Pt-Pt 6.0341.100, see the Appendix 2 for more information). Titration was completed when the current became equal to the background current (usually around

0.015 μA). The background current value corresponding to the equivalence point was established every day before the titrations.

The random effects on the titration equivalence point are taken into account by the uncertainties of the Γ factors, as explained in section 3.1. The uncertainty contribution of the possible systematic effects was estimated as ± half of the drop of titrant (assuming rectangular distribution), whereby the drop mass is estimated as 0.0105 g of titrant. This leads to standard uncertainty estimate of 0.0030 g, which is a conservative estimate, because it is possible (and was used in the experiments) to dispense the titrant in amounts approximately equal to a tenth of a drop. This way the method is more precise than usual volumetric methods. The magnitude of this uncertainty estimate covers the human factor (deviation from the point where the operator considers that the equivalence has been reached), the possible uncertainty of the background current as well as the possible uncertainty of the reading of the amperometric device used for equivalence point determination. In calculations this uncertainty is divided by the respective titrant mass and is assigned as standard uncertainty to the respective F factors corresponding to the equivalence point uncertainty.

After titration the syringe was weighed again to determine the consumed titrant mass. Seven parallel measurements were carried out according to the described procedure and the average result was used as the titrant concentration.

3.3.4. Sampling and sample preparation

Samples were taken and prepared in 10 cm^3 glass flasks with ground joint stoppers (standard ground glass stoppers). Flasks were calibrated before at different temperatures to account for the expansion/contraction of the flasks. Seven parallel samples were taken as follows:

a) The flask was filled by submerging it under the water to be measured. Every care was taken to avoid air bubbles in the flask.
b) 0.2 cm^3 of $MnSO_4$ solution (2.1 mol dm^{-3}) and 0.2 cm^3 of the alkaline KI solution was added with previously calibrated glass syringes (250 μl, Hamilton) to the bottom of the glass flask simultaneously (an equal amount of water was forced out of the flask). Care was taken in order not to introduce air bubbles when adding those solutions.
c) The flask was stoppered with care to be sure no air was introduced. The contents of the flask were mixed by inverting several times. The presence of possible air bubbles was monitored. The sample was discarded if any air bubble was seen. A brownish-orange cloud of $Mn(OH)_3$ precipitate appeared. The precipitate was let to form until it was settled down according to reaction 1.
d) The solution was then acidified by adding 0.2 cm^3 of H_2SO_4 solution (5.3 mol dm^{-3}) with another syringe (250 μl, Hamilton) below the solution surface. It is very important that all the precipitate formed stays in the flask.

Under acidic conditions Mn^{3+} ions oxidize iodide to iodine, which eventually forms I_3^- ions with the excess of KI.

The flask was stoppered again and mixed until the precipitate was dissolved. At this stage the air bubbles do not interfere anymore.

3.3.5. Titration of the sample with the $Na_2S_2O_3$ titrant

Before the start of the actual titration about 80–90% of the supposed amount of the titrant ($Na_2S_2O_3$, 0.0015 mol kg^{-1}) is added to the titration vessel from a pre-weighed plastic syringe. The formed iodine solution is transferred quantitatively to the titration vessel (to minimize evaporation of iodine) and titrated to the endpoint amperometrically as it has been discussed in section 3.3.3. This approach – so-called pre-titration – allows ca 80% of the iodine to react immediately and is a powerful tool in helping to minimize the volatilization of iodine during titration. The remaining small extent of iodine volatilization is taken into account by a correction.

After reaching the end point the titration syringe was weighed again. The amount of the consumed titrant was determined from mass difference. Seven parallel titrations were carried out.

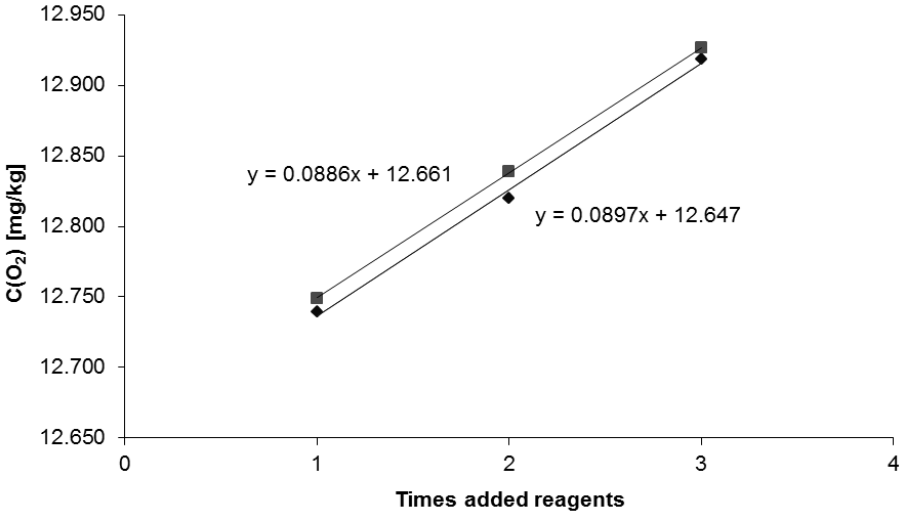
3.3.6. Determination of the correction for oxygen introduced from the reagents

The concentration of DO in the reagents is low and the amount of the reagents is small. Nevertheless the amount of oxygen introduced by the reagents is on an average around 1 μg, which is significant compared to the amounts of oxygen involved in this work. Therefore this amount of oxygen has to be taken into account. In order to do this with minimal additional uncertainty it is important that the amount of oxygen in the reagents is as reproducible as possible.

There are two possible approaches for achieving reproducible oxygen content of the reagents: (1) use reagents where the oxygen content has been decreased to a minimum (deoxygenated reagents) or (2) use reagents saturated with air. In principle it would be desirable to use reagents with DO content as low as possible. Initially this approach was taken. During the experiments it was discovered that the oxygen content in the reagents was highly variable. This caused high uncertainty of the correction term (even though its magnitude was small). One of the reasons might be contamination of the reagents by atmospheric oxygen during transfer to the sample bottle. Reagents saturated with air (which in turn was saturated with water vapor) were then taken into use. Although the determined magnitude of the correction term with such reagents was larger, its stability (reproducibility of parallel measurements) was significantly better. This led to ca two times lower combined standard uncertainties

of determined oxygen content in samples. Air-saturated reagents are immune to contamination by air oxygen.

There are several ways for accounting for the effect caused by the reagents. In this work addition experiments were used. From the same sample different subsamples were collected at the same time and different amounts of the reagents were added to determine the amount of oxygen that is introduced with the reagents. Reagent solutions were added one to three times (different amounts) to consider not only the oxygen that was in the reagent solutions but also from the procedure itself (sample contamination). The concentration of DO found in the sample was plotted against times of added reagent solutions. The correction (CF_{O2}) was found from the slope of the graph, see the Graph 3.



Graph 3. Curves from the adding tests (20.02.12).

Fourteen experiments were made for determination CF_{O2}. Each determination was made with three points. The concentration of DO in reagents depends on atmospheric pressure. Therefore all the obtained slope values were converted to the normal (sea-level) pressure. Two of the resulting graphs were strongly non-linear (relative standard deviation of linear regression slope was above 20%) and these were left out. The remaining 12 results (obtained on 7 different days) were evaluated for agreement with the Grubbs test [38] and no disagreeing results were found. CF_{O2} is found as the average of the values from Table 1 (last column). Its value is 0.0940 mg kg^{-1} (corresponding to the normal pressure) with standard deviation 0.0068 mg kg^{-1}. This standard deviation also accounts for the variability of the amount of added reagents. Although the mean value of CF_{O2} is used as correction the standard deviation of the single results (not the mean) is used as its uncertainty estimate, because this uncertainty takes into

account the variability of CF_{O2} and is not averaged during the measurements in any way.

Each time the correction was used it was recalculated to the actual atmospheric pressure at the location of the measurement. Atmospheric pressure was measured by digital barometer PTB330 (Ser No G37300007, manufactured by Vaisala Oyj, Finland).

Table 1. Results of reagents adding tests.

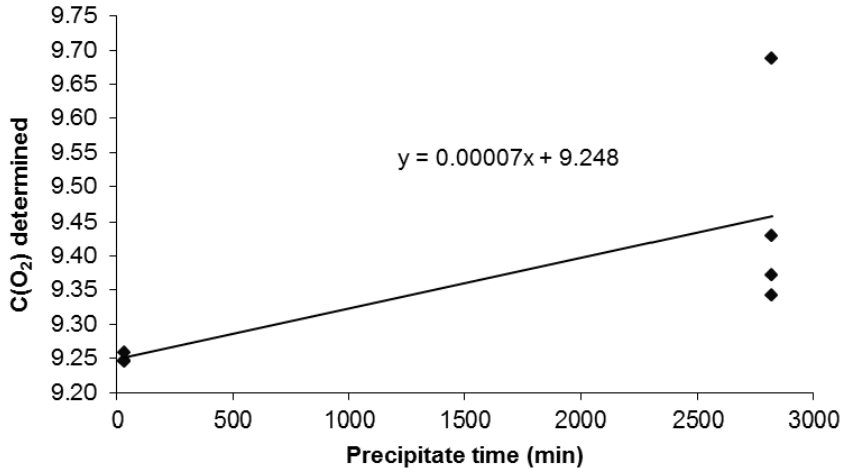
Date	b_1[a]	b_0[a]	$s(b_1)$[a]	$s(b_0)$[a]	C_{O2}Ref[b]	Δ[c]	P (Pa)	St.dev.[d]	CF_{O2} (norm)
10.10.11	0.0862	9.0116	0.0074	0.0161	9.01	0.00	99896	9%	0.087
14.10.11	0.0941	9.2034	0.0088	0.0189	9.17	–0.04	101677	9%	0.094
24.10.11	0.0983	9.2494	0.0048	0.0103	9.23	–0.02	102394	5%	0.097
	0.0897	9.2707	0.0046	0.0099	9.23	–0.04	102394	5%	0.089
28.11.11	0.1069	9.2171	0.0152	0.0327	9.20	–0.02	102054	14%	0.106
	0.1065	9.2131	0.0134	0.0289	9.20	–0.01	102054	13%	0.106
31.11.11	0.0912	9.0622	0.0077	0.0166	9.03	–0.03	100187	8%	0.092
	0.0920	9.0629	0.0061	0.0132	9.03	–0.03	100187	7%	0.093
23.01.12	0.0979	9.0105	0.0159	0.0344	9.00	–0.01	100057	16%	0.099
	0.0841	9.0305	0.0116	0.0250	9.00	–0.03	100057	14%	0.085
20.02.12	0.0897	12.6467	0.0052	0.0113	12.66	0.01	100677	6%	0.090
	0.0886	12.6608	0.0005	0.0010	12.66	0.00	100677	1%	0.089

[a] Slope (b_1) and intercept (b_0) of the linear regression and their standard deviations.
[b] reference values of DO obtained from ref 13 (in mg kg^{-1}).
[c] difference between the calculated reference value and b_0. These values should have same magnitude while b_0 corresponds to situation when reagents are not added (DO concentration in pure sample).
[d] relative standard deviation of linear regression.

3.3.7. Determination of parasitic oxygen

In order to determine the amount of oxygen introduced to the sample through the junction between the stopper and the flask neck (input quantity Int_{O2}) seven subsamples were collected at the same time and the reagents ($MnSO_4$ solution and alkaline KI solution) were added. Three of them were titrated on the same day. The remaining four were titrated two days later. The mass of DO found in the sample was plotted against the precipitation time. The mass of the introduced oxygen per minute was found as the slope of the Graph 4. The amount of parasitic oxygen introduced was found as ca 0.00007 mg kg^{-1} min^{-1}. The precipitation time for the analysis is different and ranges from few tens of

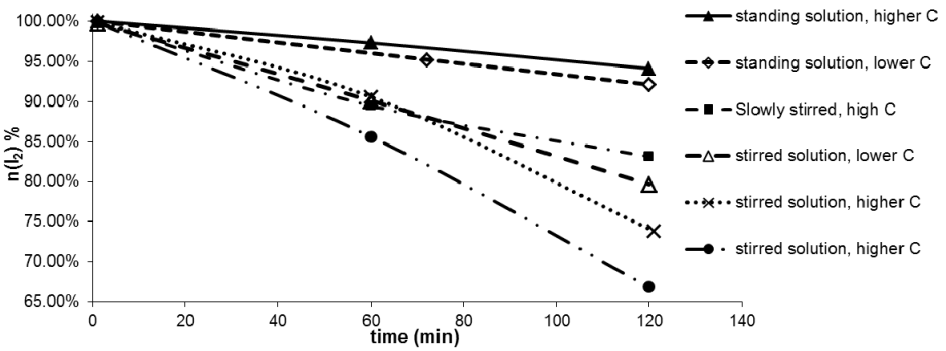
minutes to slightly more than an hour, so the content of intruded oxygen can be estimated to be in the range of 0.0015 to 0.0050 mg kg^{-1} during the precipitation time. This effect is small compared to the overall repeatability of the measurement. The exact mechanism of this process is not known, the determination of this effect is very uncertain and the precipitation time also differs widely. Therefore, based on recommendations from ref 39 it was decided not to correct for this effect but to assign the value of 0 mg kg^{-1} to Int_{O2} and take this effect into account entirely as an uncertainty contribution of ±0.005 mg kg^{-1}.



Graph 4. Determination of parasitic oxygen (Int_{O2}).

3.3.8. Iodine volatilization

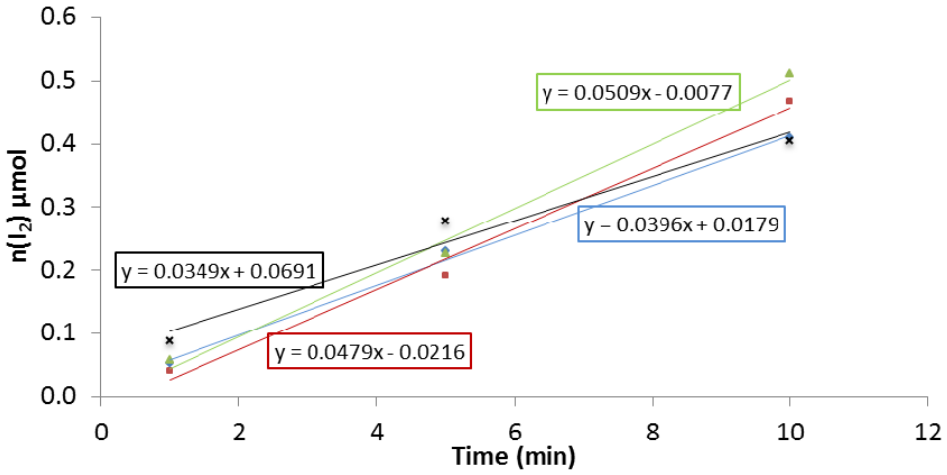
Experiments to determine the iodine volatilization amount at different experimental conditions (stirred vs standing solution and high (ca 2.4 mmol kg^{-1}) vs low (ca 0.5 mmol kg^{-1}) concentration) were carried out. As it is seen from the Graph 5, the largest effect on iodine volatilization is stirring. Also the concentration of iodine in the solution influences volatilization, but this effect is not that large and it does not come out that clearly.



Graph 5. Stirring and concentration effect on iodine volatilization.

In this procedure in the case of titration of the sample it is possible to minimize the volatilization by adding about 80–90% of the expected titrant consumption into the titration vessel before transferring the iodine-containing sample solution to the titration vessel (so-called "pre-titration"). This way the main part of the iodine reacts immediately, significantly minimizing volatilization. At the same time, evaporation of iodine occurs during transfer of the iodine solution formed from the sample into the titration vessel and this has to be taken into account also. The pre-titration approach is not possible in the case of determination of the titrant concentration because there it is necessary to stir the solution containing iodate, iodide and sulphuric acid properly before starting the titration. If this is not done then thiosulphate can react directly with iodate, not with iodine and the reaction loses its stoichiometry. For both titrations the volatilization has been taken into account by introducing two corrections, $n_{I2\_vol\_s}$ and $n_{I2\_vol\_t}$, for titration of the sample and standardizing of the titrant, respectively.

For evaluating the effect of iodine volatilization on titrant standardization four parallel measurements of a solution of 5 ml with iodine concentration of 1.9 μmol g^{-1} were made by keeping them for different times, 1, 5 and 10 minutes while stirring at 800 rpm (PTFE stirrer bar: length 21 mm, diameter 6 mm). The results were plotted as iodine loss (in μmol) against time (see the Graph 6) and the estimates for the loss of iodine in one minute were found as the slopes of the four graphs: 0.051, 0.040, 0.048, 0.035 μmol min^{-1}. The average iodine loss is thus 0.043 μmol min^{-1} with standard deviation of 0.007 μmol min^{-1}.



Graph 6. Determination of iodine volatilization.

The titration time during standardization ranges from 30 s to 60 s. The average time of 45 s was used as the estimate of titration time. So, the iodine volatilization during the standardization $n_{I2\_vol\_t}$=0.0325 µmol and it has two uncertainty components: repeatability of the average iodine loss and time, which is ±15 seconds according to ±0.008 µmol iodine.

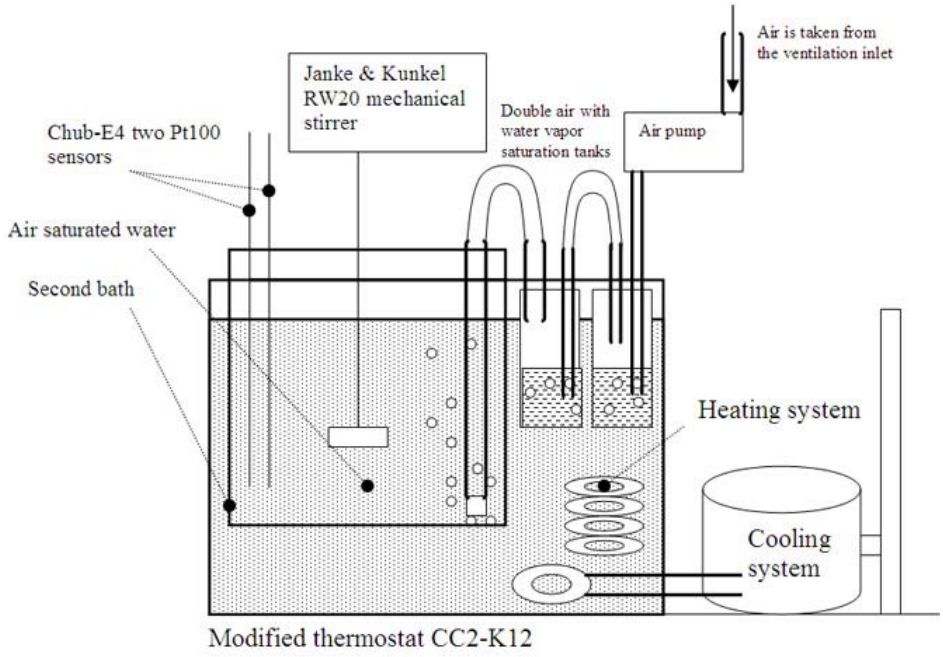
For evaluating the effect of iodine volatilization on titration of the sample, experiments on two different days were done, 7 replicates on both days. Every experiment consisted in titration of ca 10 ml of iodine solution with concentration of 0.5 µmol g^{-1} (the concentration of iodine in processed sample solutions is similar) prepared from KIO_3 into the sample type of bottle that was used for sample collecting and processing. This solution was transferred into the titration vessel in a similar way as was used for titration of the samples and was titrated (using pre-titration). The difference of the amounts of initially added iodine and iodine calculated from titration data gave the amount of volatilized iodine. The average amount of volatilized iodine by titrating the sample $n_{I2\_vol\_s}$ was found as 0.0116 µmol with the standard deviation of 0.0014 µmol, which is accounted as $u(n_{I2\_vol\_s})$ (all results are brought in Table 2).

Table 2. The absolute (in μmol) and relative (in %) losses of iodine during titration mimicking the titration of the sample.

Date	$\Delta n(I_2)$ μmol	$\Delta n(I_2)$ %
19.04.2012	0.01036	0.20%
	0.01098	0.22%
	0.01167	0.23%
	0.01074	0.22%
	0.01281	0.25%
	0.01079	0.21%
	0.01117	0.21%
27.04.2012	0.01365	0.23%
	0.01409	0.23%
	0.01134	0.20%
	0.01155	0.19%
	0.00866	0.14%
	0.01105	0.18%
	0.01284	0.21%
Average	**0.0116**	**0.21%**
St.dev	**0.0014**	**0.026%**

3.4. Saturation method for obtaining the reference DO values

Air-saturated fresh pure (MilliQ) water (at constant humidity and temperature) was used as reference medium for validating the method. The water was aerated until equilibrium was attained. The saturation medium was created in a modified (added a second bath) thermostat CC2-K12 (Peter Huber Kältemaschinenbau GmbH, Germany). See the Scheme 1 and the photo series in Appendix 1. The air used for saturation was taken from the air inlet situated on the roof of the building. The air flow velocity during calibration was around 1 dm^3 min^{-1}. The ordinary aquarium spray was used (at depth of 13 cm). The estimated diameter of the bubbles was between 0.8 to 1.8 mm.



Scheme 1. Thermostat CC2-K12 with additional bath, stirrer and thermometer.

The double-bath thermostat provides good temperature stability (see Table 3).

Table 3. Temperature stability test within 10 minutes before the sampling.

Temperature	**30°C**	**25 °C**	**20 °C**	**15 °C**	**10 °C**	**5 °C**
	29.816	24.826	19.925	15.004	10.074	5.053
	29.810	24.824	19.926	15.002	10.073	5.054
	29.808	24.829	19.926	14.999	10.065	5.054
	29.808	24.826	19.925	14.999	10.066	5.057
	29.811	24.828	19.925	15.000	10.069	5.057
	29.812	24.832	19.923	14.998	10.065	5.053
	29.811	24.843	19.917	14.999	10.067	5.053
	29.809	24.840	19.923	14.997	10.067	5.048
	29.811	24.837	19.923	15.000	10.067	5.050
	29.816	24.837	19.921	15.004	10.068	5.054
St.dev	**0.0028**	**0.0065**	**0.0029**	**0.0023**	**0.0031**	**0.0027**

In this case the maximum standard deviation has been taken as the standard uncertainty ($u(T_{\text{instab}})$=0.0065 K). Atmospheric pressure was measured by digital barometer PTB330 (Ser No G37300007, manufactured by Vaisala Oyj, Finland,

calibrated by manufacturer 19.09.2011) with uncertainty $u(p_{cal})$ = 7 Pa (k = 2). The air bubbled through the second bath was saturated with water vapor by passing it through two saturation bottles (both immersed in the same thermostat). The level of air humidity after the second saturation vessel was measured using digital hygrometer Almemo 2290–8 with sensor ALMEMO FH A646 E1C (manufacturer AHLBORN Mess- und Regelungstechnik GmbH). The humidity of the air bubbled through the water in the second bath was never lower than 95% RH. The uncertainties of all relative humidity measurements are ± 5 %RH (k = 2). The CO_2 content of the air was measured during calibration by Vaisala CARBOCAP® CO_2 Transmitter Series GMP 222 (SN: X0150001, manufactured by Vaisala, Finland). The evaluated uncertainty of the CO_2 concentration was ± 100 ppm (k = 2). The temperature of the measurement medium was measured by reference digital thermometer Chub-E4 (model nr 1529, serial No A44623, manufacturer Hart Scientific) with two Pt100 sensors. The uncertainties of all temperature measurements are ± 0.02 °C (k = 2 calibrated by the Estonian NMI, AS Metrosert on May 2011).

3.5. Differences between gravimetric Winkler carried out in syringes and in flasks

The main procedural differences between SGW and FGW are listed in Table 4. FGW is developed to decrease the measurement uncertainty, so mainly the changes in FGW procedure are made for it.

Table 4. Differences between two gravimetric Winkler method procedures.

Method characteristic	**SGW**	**FGW**	**Remarks**
Potassium iodate solution preparation	Volumetrically using a volumetric flask (1 dm^3)	Gravimetrically by consecutive dilutions	Uncertainty was decreased by ca 2 times
Titration end-point detection	Starch	Amperometric (current between two Pt electrodes decreases to background current when all iodine is titrated)	Uncertainty decreased from 0.020 g (in SGW) to 0.0032 g (in FGW)
Titration vessel	Capped with plastic caps	Open vessel	Open vessel increases iodine volatilization, but caps are impractical to use because of the electrode in case of FGW
Iodine volatilization	Determined with separate experiment, accounted as an uncertainty source	Determined with separate experiment, accounted as a correction (with an uncertainty)	Because iodine volatilization is more pronounced in FGW, it was taken into account as a correction

Table 4. Continuation

Method characteristic	**SGW**	**FGW**	**Remarks**
$Na_2S_2O_3$ titrant concentration	0.0025 mol kg^{-1}	0.0015 mol kg^{-1}	Titrant can be added more precisely when using a titrant with lower concentration (influence of the drop volume is smaller)
Sampling and sample treatment	10 cm^3 glass syringes with PTFE plungers, sample was aspirated into the pre-weighed syringe, the syringe was weighed again with sample	10 cm^3 glass flasks, calibrated at different temperatures, submerged under the water to be measured	The largest uncertainty contribution in SGW was uncertainty due to oxygen dissolved in the syringe plunger, so it was necessary to abandon the use of PTFE
Replicate measurements	6	7	
Oxygen in the Winkler reagents	C_{O2_reag}, determined daily with separate experiment	CF_{O2}, accounts also oxygen, that comes from the procedure of adding the reagents (average of 12 adding test results)	For decreasing the analysis time in FGW the reagents were saturated with air and its content in the reagents was assumed to be constant
Sample contamination with atmospheric oxygen	Contamination mainly from PTFE plunger, $O_{2\_syringe}$, determined with six separate experiments	Contamination through the junction between the stopper and the flask, Int_{O2}, determined separately, max 0.005 mg kg^{-1}	In FGW the contamination is minimized by using glassware only for sample processing

4. RESULTS AND DISCUSSION

4.1. Validation of the methods

Validation of the methods includes a number of tests: determination of parasitic oxygen from different sources, iodine volatilization in two different cases, weighing tests and in addition the test for trueness. For evaluation of trueness water saturated with air (below termed as saturation conditions) under carefully controlled conditions (air source, temperature, air pressure, air humidity) was used. Every trueness test consisted of taking six or seven samples (in SGW and FGW, respectively), measuring their DO concentration with those method and comparing the obtained average DO concentration with the reference DO values evaluated according to the standard ISO 5814 [13] by an empirical formula originally published by Benson and Krause [14]. The uncertainties of the reference values were calculated as detailed in the Appendix 3. The agreement was quantified using the E_n number approach [40].

The average results of 6 or 7 parallel measurements in SGW or FGW, respectively (as detailed in the experimental section) in comparison with the reference values from ref 13 are presented in Tables 5 and 6.

Table 5. Results of the SGW (in mg dm^{-3}) under different experimental conditions.

Date	**1.02.08**	**22.02.08**	**25.02.08**	**3.03.08**	**31.03.08**	**7.04.08**	**9.04.08**	**18.04.08**
Saturation conditions	**20 °C**	**20 °C**	**25 °C**	**5 °C**	**15 °C**	**20 °C**	**20 °C**	**20 °C**
C_{O2}**SGW**	9.24	8.78	8.06	12.31	10.06	8.97	8.94	8.96
$U(C_{O2}$**SGW**$)$ [a]	0.09	0.08	0.10	0.13	0.13	0.10	0.14	0.10
$U(C_{O2}$**SGW**$_{rel})$	0.97%	0.91%	1.24%	1.06%	1.29%	1.11%	1.57%	1.12%
C_{O2}**Ref**	9.20	8.79	8.10	12.41	10.17	8.99	8.92	8.95
$U(C_{O2}$**Ref**$)$[a]	0.06	0.06	0.06	0.08	0.06	0.06	0.06	0.06
Δ[b]	0.04	–0.01	–0.04	–0.10	–0.11	–0.02	0.02	0.01
E_n[c]	0.4	–0.1	–0.3	–0.7	–0.7	–0.2	0.1	0.1

[a] Expanded uncertainty at $k = 2$ level.
[b] $\Delta = C_{O2}SGW - C_{O2}Ref$.
[c] The E_n values are calculated and interpreted as explained in ref 40: $|E_n| \leq 1$ means agreement, $|E_n| > 1$ means disagreement.

As it is seen from the Tables 5 and 6, the agreement between the titration methods and the saturation values in the concentration range from 7 to 13 mg dm^{-3} (temperature range 30 °C to 5 °C) is very good: the absolute values of E_n numbers [40] are below 1 in all cases. Particularly good agreement with reference value is found in case of FGW results.

Table 6. Results of the FGW in comparison with the reference values obtained from ref 13 (in mg dm^{-3}) under different experimental conditions.

Date	**15.03.12**	**15.03.12**	**20.02.12**	**30.01.12**	**23.01.12**	**16.01.12**	**5.01.12**	**3.01.12**	**2.01.12**	**30.12.11**	**14.11.11**	**11.11.11**	**28.10.11**	**14.10.11**
Saturation conditions	**KCl 0.01M, 25°C**	**KCl 1M, 25°C**	**5°C**	**25°C**	**20°C**	**15°C**	**30°C**	**25°C**	**15°C**	**20°C**	**10°C**	**5°C**	**20°C**	**20°C**
C_{O2}**FGW**	8.298	6.172	12.680	8.538	8.999	10.052	7.286	8.176	9.941	8.876	11.241	12.968	9.189	9.180
$U(C_{O2}\text{FGW})^a$	0.028	0.023	0.035	0.025	0.028	0.028	0.024	0.025	0.029	0.026	0.031	0.034	0.028	0.026
$U(C_{O2}\text{FGW}_{rel})$	0.34%	0.38%	0.28%	0.30%	0.31%	0.28%	0.34%	0.31%	0.29%	0.29%	0.28%	0.27%	0.31%	0.29%
C_{O2}**Ref**	8.310[d]	6.197[d]	12.698	8.542	8.999	10.052	7.276	8.164	9.942	8.863	11.218	12.949	9.190	9.167
$U(C_{O2}\text{Ref})^a$	0.100[e]	0.100[e]	0.062	0.065	0.062	0.062	0.061	0.062	0.061	0.061	0.062	0.063	0.063	0.063
Δ^b	–0.012	–0.025	–0.017	–0.004	0.000	0.000	0.011	0.012	–0.001	0.013	0.022	0.019	–0.001	0.013
En^c	–0.1	–0.2	–0.2	–0.1	0.0	0.0	0.2	0.2	0.0	0.2	0.3	0.3	0.0	0.2

[a] Expanded uncertainty at $k = 2$ level. The number of effective degrees of freedom varied from 50 to 75, depending on conditions (see ref IV for details), therefore this uncertainty roughly corresponds to 95% confidence level.
[b] $\Delta = C_{O2}\text{FGW} - C_{O2}\text{Ref}$.
[c] The E_n values are calculated and interpreted as explained in ref 40: $|E_n| \leq 1$ means agreement, $|E_n| > 1$ means disagreement.
[d] Reference value is calculated using values from ref 41.
[e] Uncertainty of the reference value is estimated to be larger due to different experimental conditions and due to using an additional function taking into account the salting out effect.

4.2. Measurement uncertainties

Comprehensive uncertainty evaluation was made for both methods. As it is seen from Tables 5 and 6, depending on the exact measurement conditions the expanded uncertainty at $k = 2$ level of the methods (at saturation conditions) varies in the range of 0.08 – 0.13 and 0.023 – 0.035 mg dm^{-3} in SGW and FGW, respectively. The uncertainty budgets of the two developed methods together with the relative uncertainty contributions of the input quantities (expressed in %) are presented in Figures 1 and 2, respectively. The uncertainty contributions differ somewhat from measurement to measurement and the indicated contributions refer to a (rather average) particular measurement. The uncertainties of DO concentration of the two methods differ by more than three times and because of that the relative uncertainty contributions are not in all cases useful for comparison. Therefore in the discussion also the absolute uncertainty components (in $k = 2$ confidence level) of the input quantities are used, related directly to the dissolved oxygen concentration and expressed in mg dm^{-3}.

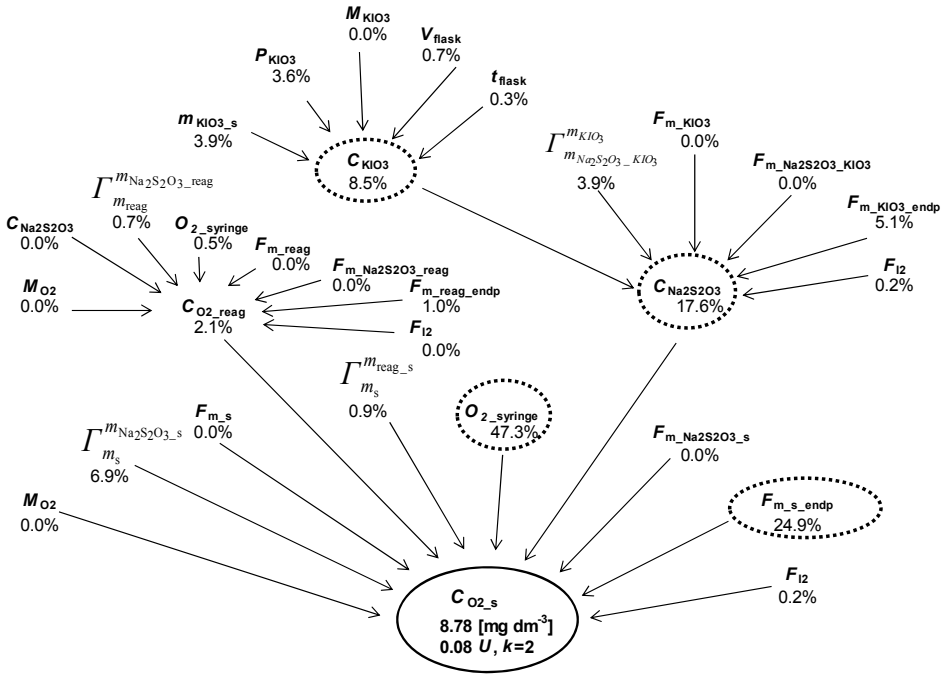


Figure 1. Uncertainty budget of the SGW in 22.02.2008.

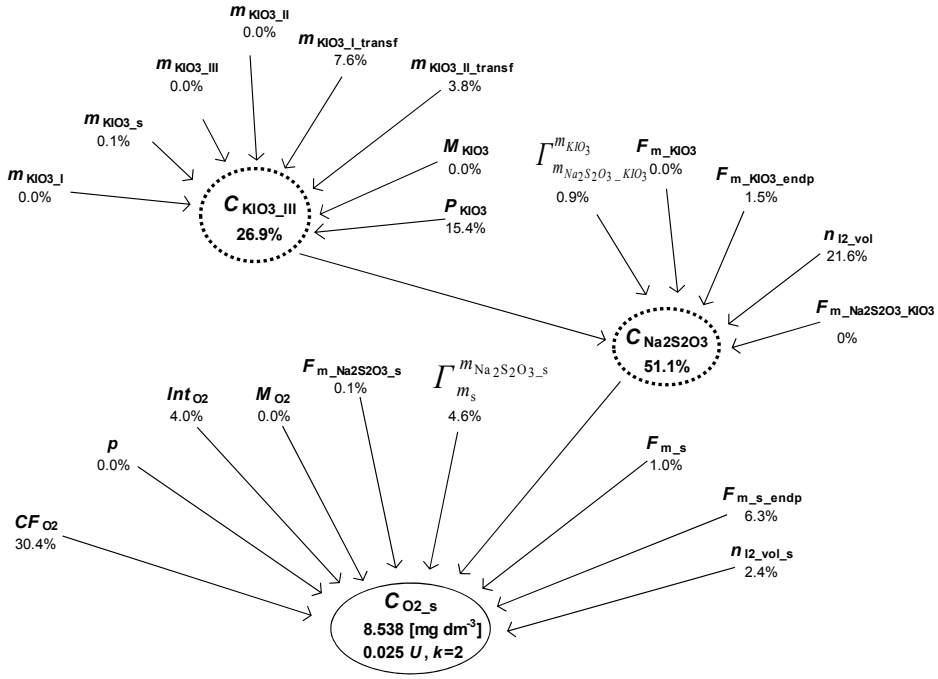


Figure 2. Uncertainty budget of the FGW in 30.01.2012.

The absolute uncertainty component of KIO_3 solution is 0.024 mg dm^{-3} and 0.013 mg dm^{-3} in the SGW and FGW, respectively. The decrease of the uncertainty is due to purer standard substance and gravimetrically prepared solutions. Nevertheless, because the overall uncertainty of the FGW method is significantly lower the relative uncertainty components are 8.5% and 26.9% in the SGW and FGW, respectively. Consecutive dilutions of the KIO_3 solutions prepared gravimetrically in FGW were used for minimizing the uncertainty caused by weighing small amounts of solid standard substance (as was done in the case of SGW). Although this way one more uncertainty source was introduced in FGW – evaporation of water from transferred stock solutions ($m_{KIO3\_I\_transf}$ and $m_{KIO3\_II\_transf}$) − the uncertainty component is still lower. In both methods the purity of KIO_3 was one of the main contributors.

The uncertainty of titrant concentration accounts for 17.6% and 51.1% of the uncertainty in the SGW and FGW, respectively. The respective absolute uncertainty components are 0.035 mg dm^{-3} and 0.018 mg dm^{-3}, being ca two times different. The most important uncertainty contributions to $C_{Na2S2O3}$ are distinctly different in the case of SGW and FGW. In SGW the main contributors are C_{KIO3}, uncertainty due to titration end-point and repeatability of the titrant standardization (8.5%, 5.1% and 3.9% of the overall uncertainty, respectively). In FGW also about half of this uncertainty was caused by C_{KIO3}, but remaining

half is covered by uncertainty due to iodine volatilization during the titration. In SGW this uncertainty source was small because of coating the titration vessel.

The most important uncertainty contributions in SGW are uncertainty due to oxygen dissolved in the PTFE syringe plunger $O_{2syinge}$ (47%) and the uncertainty of titration end-point determination (25%). In the case of FGW the former is largely eliminated by the different sampling approach. The latter is minimized in FGW by amperometric end-point determination instead of starch. This influence is remarkable: the absolute uncertainty component due to end-point determination decreased about 6 times, from 0.042 mg dm^{-3} to 0.0064 mg dm^{-3}. In FGW the uncertainty contributor $O_{2syinge}$ is eliminated by using glass flask for sample processing, but instead of this in FGW component Int_{O2} is introduced. This quantity accounts for sample contamination when using flasks. $O_{2syinge}$ is huge compared to Int_{O2} and that is why it is taken into account as a correction, but the Int_{O2} is accounted for only as uncertainty source. Uncertainty introduced by contamination of the sample is 47% and 4% of the overall uncertainty for SGW and FGW, respectively. When expressed as absolute uncertainty components, 0.058 mg dm^{-3} and 0.0051 mg dm^{-3}, respectively, it can be see that the uncertainty due to contamination of the sample decreased by 11 times when moving from SGW to FGW.

In SGW the DO concentration in Winkler reagent solutions was determined daily. This stage was time-consuming and it was eliminated in FGW by using reagents saturated with air. So in FGW this contributor is displaced against CF_{O2}, which is a constant and involves determination of this parameter as well as the real change in the DO concentration and it also saves about 2 hours analysis time. These contributors correspond about 0.012 mg dm^{-3} and 0.014 mg dm^{-3} of the all uncertainty, C_{O2_reag} and CF_{O2}, respectively, demonstrating a slight increase of the uncertainty contribution due to oxygen dissolved in Winkler reagents when moving from SGW to FGW.

4.3. Comparison with the uncertainties of other Winkler methods published in the literature

The reliability of the Winkler method results is mostly discussed in terms of repeatability and agreement with other methods' data. Table 7 summarizes the available literature data. The last column of the table indicates the meaning of the accuracy estimate. There is a large variety of the ways how accuracy was estimated.

Table 7. Accuracy information of DO measurement results by the Winkler method from different literature sources. Accuracies estimated as repeatabilities are given in italic.[a]

Reference	Accuracy estimate (mg dm^{-3})	Remarks, the meaning of the accuracy estimate
Carpenter et al. [29]	*0.004*	Repeatability recalculated to the saturated DO concentration at 20 °C
Carritt et al. [18]	*0.07*	The precision or repeatability that can be achieved by a good analyst during the replication of certain standardization procedures.
Standard ISO 5813 [16]	*0.03–0.05*	Repeatability, 4 separate laboratories, batch standard deviation
Standard methods for wastewater [42]	*0.02*	Repeatability in distilled water. In wastewater the repeatability is around 0.06 mg dm^{-3}
Labasque et al. [19]	0.068	Within-lab reproducibility over ten consecutive days
Fox et al. [21]	0.015–0.115	Combined standard uncertainty, re-estimated in this work. [II]
Krogh [20]	0.135	Combined standard uncertainty, re-estimated in this work. [II]
Whitney [22]	0.11	Combined standard uncertainty, re-estimated in this work. [II]
Helm et al. [III]	0.04–0.07	Method SGW in this work. Combined standard uncertainty, comprehensive uncertainty analysis
Horstkotte et al. [43]	*0.02–0.15*	Repeatabilities at 1.3 – 6.96 mg L^{-1} dissolved O_2 levels, in-line monitoring
Langdon [8]	*0.005*	0.15 µmol kg^{-1}, stated as a precision. Calculations with data presented in the article gave average relative repeatability 0.35% that corresponds on DO concentration of 9 mg dm^{-3} to 0.03 mg dm^{-3}.
Sahoo et al. [23]	*0.00014–0.11*	The repeatability in measurement at mg L^{-1} levels is 0.11 mg L^{-1} with RSD 1.9% and at 10 µg L^{-1} level is 0.14 µg L^{-1}, RSD 1.4%
Helm et al. [IV]	0.012–0.018	Method FGW in this work. Combined standard uncertainty, comprehensive uncertainty analysis

[a] All repeatability and reproducibility estimates are given as the respective standard deviations.

From the point of view of practical usage of the methods the most useful accuracy characteristic is the combined measurement uncertainty taking into account all important effects – both random and systematic – that influence the measurement results. A number of authors characterize their data by repeatability [26] estimates, which by definition do not take into account any systematic effects and may give a false impression of highly accurate method. Such estimates (presented in italics in Table 7) cannot be compared with measurement uncertainties and are left out of consideration.

As it is seen from Table 6 and Table 7 the FGW described in the present work has the lowest uncertainty.

4.4. Comparison of the Gravimetric Winkler method with saturation method for calibration of DO sensors

Today calibration of electrochemical and optical sensors is generally done by using the saturation method. The reference values of DO saturation concentrations are usually found using the equation by Benson and Krause [13,14,15], which takes into account water temperature, air pressure and air humidity. For obtaining accurate results an accurate barometer, an accurate thermometer and a very stable thermostat are needed. Even with good equipment the saturation method is tricky to use and is prone to errors. One of the main issues is the super- or undersaturation. The smaller are the bubbles used for saturation the faster the saturation conditions are achieved. At the same time small bubbles may lead to supersaturation [52]. Use of the larger bubbles avoids supersaturation, but makes the time necessary for saturation long. The result is that if the operator is not patient enough the solution is undersaturated. Furthermore, it is not documented in refs [13,14,15] what was the geometry of the nozzle and the bubble size, but these are important parameters of the saturation method. If uncertainty due to the possible super- or undersaturation is carefully taken into account then the resulting uncertainty is by 2–3 times higher than the uncertainty of the gravimetric Winkler method.

When measuring DO concentration with optical or amperometric sensors in water with high salinity, e.g. seawater, then calibration should be carried out in water with similar salinity. This is very difficult to do rigorously with the saturation method because the available saturation values of DO concentration in seawater are significantly less accurate than the respective values in pure water. An alternative approach is to calibrate in water and apply a salinity correction, but this again introduces a substantial uncertainty from the correction. At the same time, the dissolved salts do not hinder usage of the Winkler method.

CONCLUSIONS

This work presents a highly accurate primary method for determination of dissolved oxygen concentration in water based on the Winkler titration method. Careful analysis of the relevant uncertainty sources was carried out. The method was optimized for minimizing all uncertainty sources as far as practical, resulting in the most exhaustive uncertainty analysis of the Winkler method ever published. More than 20 uncertainty sources were found and their magnitudes evaluated. The most important uncertainty contributors are: oxygen introduced from the reagent solutions, iodine volatilization during the analysis and purity of the potassium iodate standard substance.

Depending on measurement conditions and on the dissolved oxygen concentration, uncertainties (k = 2, expanded) of the results obtained using the developed gravimetric Winkler method are in the range of 0.023–0.035 mg dm^{-3} (0.27–0.38%, relative).

SUMMARY

Dissolved oxygen (DO) content in natural waters is a very important parameter. Recent studies show decrease in DO content in several areas of world oceans. Processes leading to this decrease are not completely understood and it is very important to be able to measure DO content very accurately for studying the dynamics of these processes. Amperometric and more recently also optical oxygen sensors are widely used in DO measurements. These sensors need calibration and therefore solutions with accurate DO concentration are necessary. Oxygen is a very unstable analyte due to its chemical, physical and biological properties. For this reason it is almost impossible to prepare oxygen solutions in ordinary way by dissolving an accurately measured amount of oxygen in water. The problem can be solved by determining DO content in the calibration solutions using some primary method (i.e. method not needing calibration) that also ensures traceability to SI units. The most reliable primary DO measurement method available is the Winkler titration method. For this method several of factors limiting its accuracy were found, including the volumetric nature of the classical Winkler method. A number of modifications of the Winkler method have been proposed that should eliminate or compensate for these disadvantages. However, before the start of this work there were no publications available that would comprehensively review all the important uncertainty sources of the Winkler method and still a lot of room existed for improving the accuracy of the Winkler method. Most of the publications give repeatability of the results only. In some cases individual uncertainty sources were separately estimated. The method proposed in this work differs from the previously proposed method by its gravimetric approach, which assures lower uncertainty. Detailed analysis of the uncertainty sources and comprehensive uncertainty estimation were carried out. Experiments for determining the different influence factors were carried out, corrections were determined and uncertainty contributions for accounting these influences were estimated. As a result a detailed uncertainty budget was compiled. This budget is very useful for optimizing the function for getting more accurate measurement results. The optimization was carried out and as a result of this the gravimetric Winkler method modification for determination of DO in water giving the results with lowest available uncertainty was developed.

SUMMARY IN ESTONIAN

Kõrge täpsusega gravimeetriline Winkleri meetod lahustunud hapniku määramiseks

Lahustunud hapniku sisaldus looduslikes vetes on väga oluline parameeter. Viimasel ajal on täheldatud hapnikutaseme langust maailma ookeanide mitmetes piirkondades. Protsessid, mis selleni viivad ei ole lõpuni arusaadavad ja nende lahtimõtestamiseks on väga oluline suuta hapnikusisaldusi kõrge täpsusega mõõta. Üsna laialdaselt mõõdetakse lahustunud hapniku sisaldust vees amperomeetriliste ja viimasel ajal ka optiliste hapnikuanalüsaatoritega. Need analüsaatorid vajavad kalibreerimist ja ei ole seega kasutatavad primaarmeetoditena. Kalibreerimiseks vajalike stabiilse kontsentratsiooniga hapnikulahuste valmistamine traditsioonilisel moel on hapniku keemiliste, füüsikaliste ja bioloogiliste omaduste tõttu pea võimatu. Seega, et tagada lahustunud hapniku määramisel tulemuste jälgitavus SI ühikuteni, on tarvilik primaarmeetodi olemasolu, millega saaks kalibreerimiseks kasutatavates lahustes hapniku sisaldust kõrge täpsusega mõõta. Primaarmeetodiks lahustunud hapniku määramisel on Winkleri jodomeetriline tiitrimismeetod. Sellel meetodil on leitud rida kitsaskohti kaasa arvatud see, et klassikaliselt on tegemist mahtanalüütilise meetodiga. Kirjanduses on avaldatud terve hulk Winkleri meetodi modifikatsioone, mis peaksid selle meetodi puudusi parendama. Nende metoodikatega saadud tulemuste korrektsed, kõiki olulisi allikaid arvestavad määramatuse hinnangud aga puudusid kirjandusest enne käesoleva töö algust. Enamik kirjandusallikaid on piirdunud vaid korduvuse andmetega, mõnel juhul oli eraldi hinnatud ka üksikuid muude määramatuse allikate panuseid.

Erinevalt seni pakutud Winkleri meetodi modifikatsioonidest on käesolevas töös välja töötatud metoodika gravimeetriline tagades sellega madalama määramatuse kui senini saavutatud. Töö käigus välja töötatud metoodika jaoks viidi läbi detailne mõõtemääramatuse hindamine. Selle jaoks sooritati eksperimente mitmesuguste mõjuallikate kindlakstegemiseks, leiti nendele vastavad parandid ja määramatuste panused. Määramatuse hindamise tulemusena saadud määramatuse koond sisaldab erinevate komponentide panuseid ning on võimas abivahend meetodi optimeerimiseks ja veelgi täpsemate tulemuste saamiseks. Seda võimalust käesolevas töös ka kasutati ning selle tulemusena arendati välja Winkleri meetodi gravimeetriline modifikatsioon, mis annab seniavaldatutest madalaima määramatusega tulemusi lahustunud hapniku määramisel vees.

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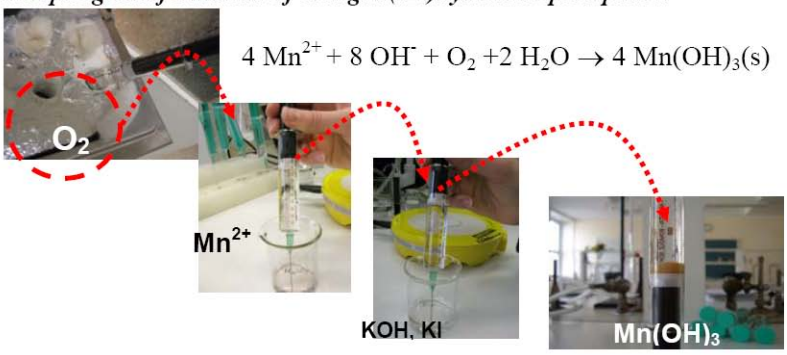
APPENDIX I

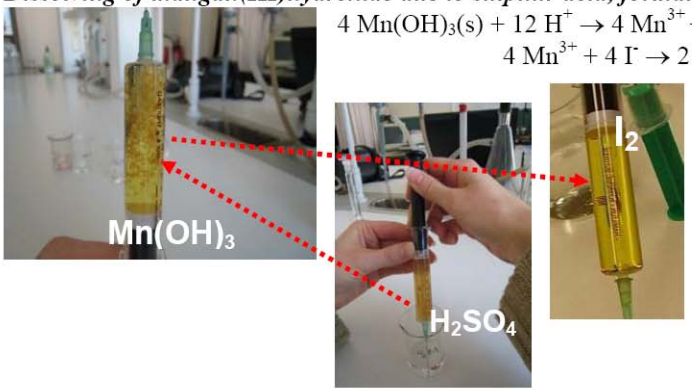
Photos of the SGW procedure

Sampling and formation of mangan(III)hydroxide precipitate:



$$4\ Mn^{2+} + 8\ OH^- + O_2 + 2\ H_2O \rightarrow 4\ Mn(OH)_3(s)$$

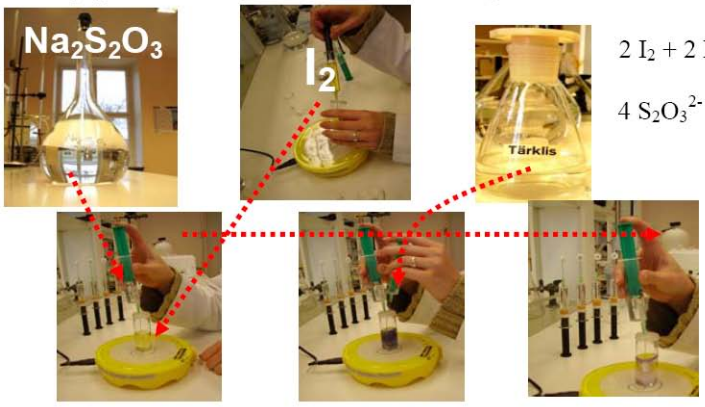
Dissolving of mangan(III)hydroxide due to sulphur acid, formation of iodine solution:



$$4\ Mn(OH)_3(s) + 12\ H^+ \rightarrow 4\ Mn^{3+} + 12\ H_2O$$

$$4\ Mn^{3+} + 4\ I^- \rightarrow 2\ I_2 + 4\ Mn^{2+}$$

Titrating of iodine solution with sodium thiosulphate:

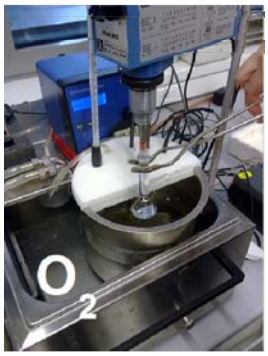


$$2\ I_2 + 2\ I^- \rightarrow 2\ I_3^-$$

$$4\ S_2O_3^{2-} + 2\ I_3^- \rightarrow S_4O_6^{2-} + 6I^-$$

Photos of the FGW procedure

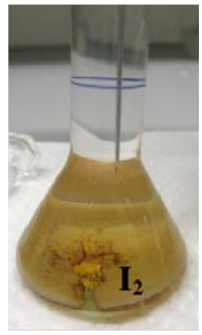
Sampling and formation of mangan(III)hydroxyde precipitate:



$$4Mn^{2+} + 8OH^- + O_2 + 2H_2O \rightarrow 4Mn(OH)_3(s)$$

Dissolving of mangan(III)hydroxyde precipitate, formation of iodine solution:

$$4Mn(OH)_3(s) + 12H^- + 4I^- \rightarrow 2I_2 + 4Mn^{2+} + 12H_2O$$
$$4Mn^{3+} + 4I^- \rightarrow 2I_2 + 4Mn^{2+}$$



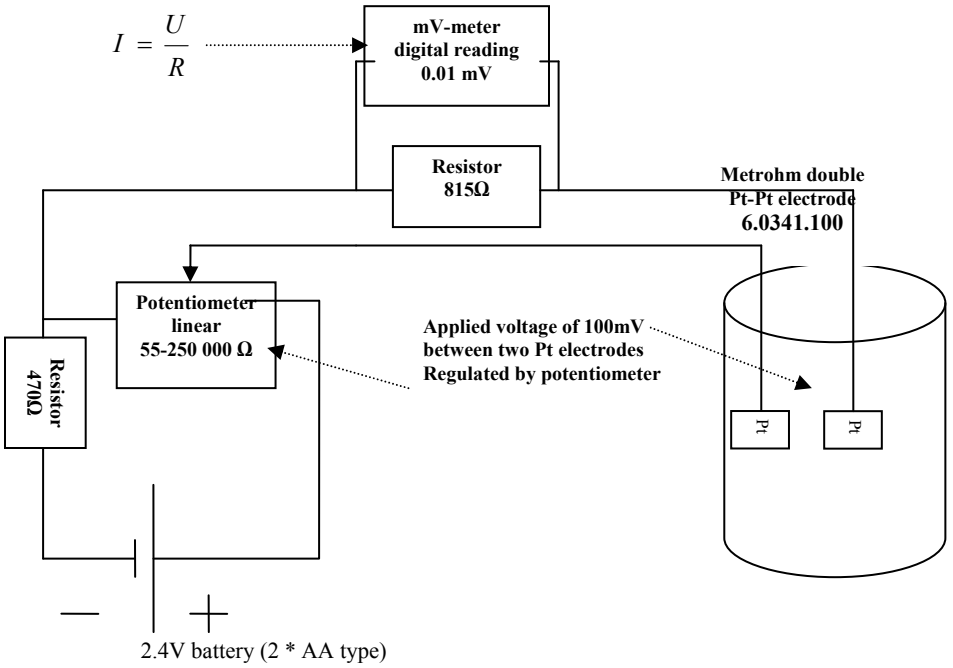
Titrating of iodine solution with sodium thiosulfate:

$$4S_2O_3^{2-} + 2I_2 \rightarrow 2S_2O_6^{2-} + 4I^-$$

APPENDIX 2

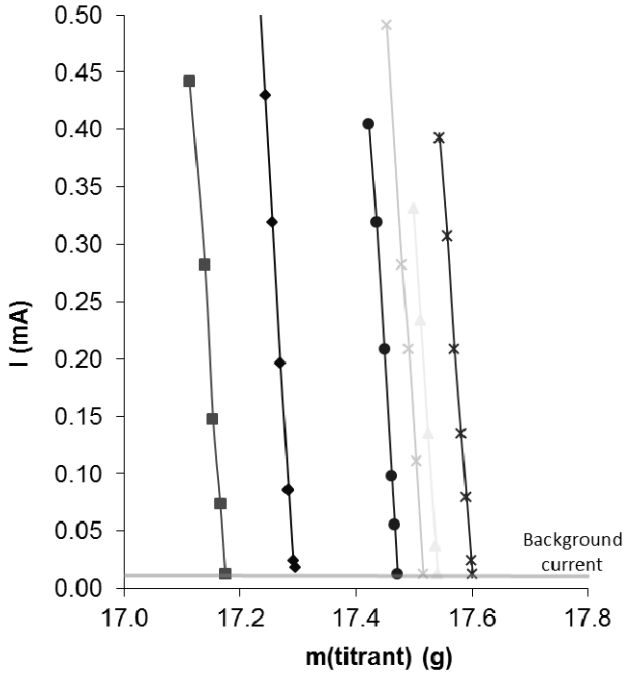
Determination of the equivalence point

Titration equivalence point was determined amperometrically by using the system shown in Scheme A1.



Scheme A1. Amperometric system for determination of equivalence point.

A voltage of 100 mV was applied between two platinum electrodes. As long as both iodine and iodide are present in solution there is non-zero current: on cathode iodine is reduced and on anode iodide is oxidized. When all the iodine has been converted to iodide the current will be equal to the background current. Near the equivalence point there is an excess of iodide in the solution and the current-limiting species is iodine. In this region the current is to a very good approximation linear with respect to the iodine concentration (see the graph A1). Therefore, by monitoring the current value it is possible to predict with very high accuracy how much titrant still needs to be added for reaching the equivalence point. This, together with the possibility of adding fractions of drops with the syringe is the reason of the low uncertainty contribution of titration end-point determination.



Graph A1. Iodine solution titration until the background current is reached.

APPENDIX 3

Measurement model in calculating the reference DO values

$C_{O2\_saturation}$ is the concentration of oxygen in air-saturated MilliQ water [mg dm^{-3}] at the measurement temperature. It is normally found using one of the various available empirical equations [15, 50]. In this work the equation A1 by Benson and Krause [14] is used. This equation is considered one of the best available and has been adopted by the standard ISO 5814 [13].

$$C_{O2\_saturation} = \exp\left(A_1 + \frac{A_2}{T + \Delta T_{instab}} + \frac{A_3}{(T + \Delta T_{instab})^2} + \frac{A_4}{(T + \Delta T_{instab})^3} + \frac{A_5}{(T + \Delta T_{instab})^4} \right) \cdot W + \Delta C_{O2\_saturation} + \Delta C_{O2\_supersat} \quad \text{(A1)}$$

where T [K] is the temperature of the water and ΔT_{instab} [K] is the term taking into account the instability of the temperature in the vessel; A_1, A_2, A_3, A_4 and A_5 are constants [14,15]. W is the pressure correction factor [13]:

$$W = \frac{p - p_{H2O} + \Delta p_{CO2}}{p_n - p_{H2O\_100\%}} \quad \text{(A2)}$$

where p [Pa] is the atmospheric pressure at measurement conditions, Δp_{CO2} [Pa] is the uncertainty of carbon dioxide content in air, p_n [Pa] is the atmospheric pressure at standard conditions and $p_{H2O\_100\%}$ [Pa] is the water vapor pressure at 100% relative humidity. It is found according to A3 [15].

$$p_{H2O\_100\%} = p_n \cdot \exp\left(B_1 + \frac{B_2}{T} + \frac{B_3}{(T)^2} \right) \quad \text{(A3)}$$

where B_1, B_2 and B_3 are constants. The pressure p_{H2O} [Pa], the real content of H_2O in air, is found experimentally (during aeration at calibration conditions).

The $C_{O2\_saturation}$ value was used as the reference value for comparing the DO concentrations found with the Winkler method: $C_{O2}\text{Ref} = C_{O2\_saturation}$.

Uncertainty estimation of the reference DO values

Uncertainty of $\Delta C_{O2\_saturation}$. Numerous tables of saturated DO concentration values have been published [13,14,15,18,44,45,46,47,48,49]. The differences between the data of different authors are generally in the order of 0.05 mg dm^{-3} [50]. It is assumed that these discrepancies come from the influence of two uncertainty sources:

(1) Uncertainty of the reference methods of determining the DO concentration [16] used for compiling the tables of published values of saturated oxygen concentrations [13,50].

(2) Uncertainty arising from the imperfect fit of the mathematical model of oxygen saturation concentrations to the data [13,50]. This can also be regarded as the uncertainties of the constants A_1 to A_5.

All these uncertainty sources are taken into account by the term $\Delta C_{O2\_saturation}$. Its value is set to zero and based on the available data its uncertainty is estimated as ± 0.05 mg dm^{-3} (k = 2) that is $u(\Delta C_{O2\_saturation})$ = 0.025 mg dm^{-3}.

Temperature *T*. This uncertainty source is caused by the limited accuracy of the thermometer used for temperature measurement and is taken into account as $u(T)$. In the case of the thermometer with uncertainty $u(T)$ = 0.01 K was used.

Temperature instability of the calibration medium ΔT_{instab}. The uncertainty due to the non-ideal temperature stability of the thermostat is taken into account by the term ΔT_{instab}. Its value is set to zero and its uncertainty is estimated as follows: $u(\Delta T_{instab})$ = 0.0065 K.

Atmospheric pressure during calibration *p*. This uncertainty source is caused by the limited accuracy of the barometer used for measuring the atmospheric pressure and is taken into account as $u(p)$. In the case of the external barometer the standard uncertainty due to calibration is 3.5 Pa. Additionally drift and reading repeatability were taken into account and the following uncertainty estimate was obtained: $u(p)$ = 5.2 Pa.

Partial pressure of water vapor p_{H2O}. The partial water vapor pressure in air saturated with water (at minimum 95% relative humidity) was measured with uncertainty ± 5% (k = *2*) at our laboratory: $u(p_{H2O})$ = 111 Pa (at temperature 20.0 °C).

Oxygen content in air Δp_{CO2}. The partial oxygen pressure in air saturated with water depends also on the content of carbon dioxide [50,51,52]. The performed experiments (during aeration, under calibration conditions) showed that the content of carbon dioxide in air varies in the range of 0.04% to 0.07%, the lowest end of this range being the standard content of CO_2 in air. The highest end of this range is possible only when the air is taken directly from the room where people are working, which is not the case with our measurements (air is taken from the ventilation inlet situated on the roof of the building). The effect of varying CO_2 content is small and thus it is not practical to correct for it. It is instead included entirely in the uncertainty estimate. The value Δp_{CO2} is set to zero and its uncertainty $u(\Delta p_{CO2})$ is conservatively estimated as 41 Pa (under the normal pressure 101325 Pa).

Supersaturation $\Delta C_{O2\_supersat}$. This component takes into account the uncertainty originating from possible supersaturation (or undersaturation). In our case the used MilliQ water was pre-saturated at level of ca 70%. At least 2.5 hours were allowed for full saturation counting from the time when the temperature of the bath was stabilized. The saturation process was monitored by optical dissolved oxygen analyzer HACH 30d with a digital resolution of 0.01 mg dm^{-3}. The possible supersaturation depends on aeration speed (over-pressure generated by the pump), the intensity of mixing and the size of bubbles. The smaller are the bubbles the higher may be the supersaturation. Unfortunately, the exact saturation conditions, including the optimal size of the bubbles are not specified in the ISO 5813 standard [16] or in the original papers [14,15]. In this work the size of the bubbles was in the range of 0.8–1.8 mm (estimated using a ruler immersed into the bath and comparing the bubble size to the ruler using photos). The standardized procedure of obtaining accurate dissolved oxygen concentrations in water from the former Soviet Union [53] contains detailed description of the saturation conditions and the bubble size according to that standard is 3 mm. The saturation values of ref [53] are in good agreement with the ISO 5813 standard [14]. The maximum difference in the temperature range 5–30 ^{o}C is ± 0.02 mg dm^{-3}. Truesdale et al claim [52] that bubbles with the diameter of 0.1 mm lead to a supersaturation of ca 0.6%. On the tentative assumption that the extent of supersaturation is linearly related to bubble

diameter it follows that when moving down from 3 mm bubbles then the supersaturation is ca 0.2% per 1 mm of bubble diameter. The smallest possible bubble diameter used in this work was 0.8 mm and this would mean ca 0.44% of supersaturation, which at 20 °C means ca 0.04 mg dm^{-3}. In order to verify this assumption a comparison between saturation conditions differing by bubble size was made using an optical dissolved oxygen analyzer HACH 30d. The difference of 0.03 mg dm^{-3} was found between the dissolved oxygen concentrations when saturation with 3 mm bubbles and 0.8 mm bubbles was compared. Thus the possible supersaturation might be as high as 0.03 mg dm^{-3}. Nevertheless it is not possible to fully rule out undersaturation and therefore the value of zero was assigned to $\Delta C_{O2\_supersat}$. Its standard uncertainty $u(\Delta C_{O2\_supersat})$ is estimated from the maximum value 0.03 mg dm^{-3} (assuming rectangular distribution) as 0.017 mg dm^{-3}.

APPENDIX 4

Uncertainty evaluation for SGW in 22.02.2008: Input quantities

Constants:

M_{KIO3}=	214.001	g/mol
M_{O2}=	31998.8	mg/mol
$M_{Na2S2O3}$=	158.1077	g/mol
$O_{2\_syringe}$=	2.108	µg

Date:
22-Feb-08
Operator:
Irja Helm, glass syringe
Preparation of the KIO_3 standard solution

$V\_KIO_3\_solution$	1.0	dm^3
$m_{KIO3(t)}$	0.2847	g
P_{KIO3}	0.9985	-
Temperature of laboratory	20.0	°C
Density of KIO_3 standard solution	0.9985	kg/dm^3
C_{KIO3}	0.0013	mol/kg

Determination of the $Na_2S_2O_3$ solution concentration

Nr	m(tare)	m(tare+ KIO_3)	m(KIO_3)	m(titr syr before)	m(titr syr after)	m(titrant)
1	21.0640	24.0118	2.9478	70.6831	61.1625	9.5206
2	21.2989	24.2152	2.9163	70.7125	61.2976	9.4149
3	21.5473	24.5004	2.9531	70.6996	61.1752	9.5244
4	22.4008	25.3645	2.9637	70.7006	61.1432	9.5574
5	21.4253	24.3728	2.9475	70.7063	61.1725	9.5338
6	21.4876	24.4346	2.9470	70.6886	61.1295	9.5591
arithmetic mean			2.9459			9.5184

Determination of the O_2 concentration in reagent solutions

Nr	m(sample syr)	m(sample syr +MnSO4)	m(sample syr + MnSO4 +KOHKI)	m(MnSO4)	m(KOHKI)	m($MnSO_4$+ KOHKI)	m(titr syr before)	m(titr syr after)	m(titrant)
1	61.7216	64.0558	66.9806	2.3342	2.9248	5.2590	70.7043	69.7661	0.9382
2	61.7769	64.1149	66.9890	2.3380	2.8741	5.2121	69.6652	68.7383	0.9269
3	61.7658	64.1048	67.0557	2.3390	2.9509	5.2899	68.6978	67.7330	0.9648
4	61.6165	63.9547	66.8452	2.3382	2.8905	5.2287	67.7328	66.8979	0.8349
5	61.4475	63.8098	66.6491	2.3623	2.8393	5.2016	66.6808	65.7932	0.8876
6	61.2394	63.5867	66.4573	2.3473	2.8706	5.2179	65.6961	64.7937	0.9024
arithmetic mean						5.2349			0.9091

Determination of the O_2 concentration in sample

Nr	m(sample syr)	m(sample syr + sample)	m(sample)	m(syr+ sample+ reag)	m (reag)	t (°C)	$t_{corrected}$ (°C)	p (Pa)	$p_{corrected}$ (Pa)	m(titr syr before)	m(titr syr after)	m(titrant)	ref C_{O2} [mg/kg]	ref C_{O2} [mg/dm³]
1	61.7176	70.9796	9.2620	71.5058	0.5262	20.10	20.0	97850	98031.3	70.7062	66.3780	4.3282	8.805	8.790
2	61.7671	71.0305	9.2634	71.5482	0.5177	20.10	20.0	97850	98031.3	70.6929	66.3896	4.3033	8.805	8.790
3	61.7578	71.0268	9.2690	71.5459	0.5191	20.10	20.0	97850	98031.3	70.6962	66.4016	4.2946	8.805	8.790
4	61.6082	70.8472	9.2390	71.3851	0.5379	20.10	20.0	97850	98031.3	70.6530	66.3558	4.2972	8.805	8.790
5	61.4564	70.7357	9.2793	71.2528	0.5171	20.10	20.0	97850	98031.3	70.7100	66.4043	4.3057	8.805	8.790
6	61.2359	70.4961	9.2602	70.9514	0.4553	20.10	20.0	97850	98031.3	70.6984	66.3975	4.3009	8.805	8.790
arithmetic mean			9.2622		0.5122							4.305	**8.805**	**8.790**

Uncertainty evaluation for SGW in 22.02.2008: Determination of C_{KIO3}

$$C_{KIO_3} = \frac{m_{KIO_3\_s} \cdot P_{KIO_3}}{M_{KIO_3} \cdot V_{flask} \cdot \rho}$$

$$\rho = a \cdot t_{flask} + b$$

Input quantities

Denotion	Uncorr value	u_c	Unit
m_{KIO3_s}	0.2847	0.00026	g
P_{KIO3}	0.9985	0.0009	%
M_{KIO3}	214.00097	0.00045	g/mol
V_{flask}	1.000	0.00038	dm^3
t_{flask}	20	1.1547	°C

Uncertainty components of input quantities

u	component	u	component	u	component	u	component	u	component	u	component
0.00016	repeatability1	0.000029	rounding1	0.00016	repeatability2	0.000029	rounding2	0.000115	linearity	0.0000007	drift
0.00087	purity										
0.00005	K	0.000015	I	0.00015	O						
0.0002309	calibration	0.0001732	filling	0.00024	temperature						
1.15470	temperature										

Input quantities

Denotion	Corr value	Unit	u_c	Relative
m_{KIO3_s}	0.2847	g	0.00026	0.090%
P_{KIO3}	0.9985	%	0.00087	0.087%
M_{KIO3}	214.0010	g/mol	0.00045	0.000%
V_{flask}	1.0000	dm^3	0.00038	0.038%
t_{flask}	20.0000	°C	1.15470	5.774%
C_{KIO3}	**0.0013304**	**mol/kg**	**0.0000018**	**0.13%**

Uncertainty evaluation using the Kragten approach

m_{KIO3_s}	P_{KIO3}	M_{KIO3}	V_{flask}	t_{flask}	
0.285	0.285	0.285	0.285	0.285	
0.999	0.999	0.999	0.999	0.999	
214.0	214.0	214.0	214.0	214.0	
1.0	1.0	1.0	1.0	1.0	
20.000	20.000	20.000	20.000	20.1	
0.00133	0.00133	0.00133	0.00133	0.00133	Value
0.00000	0.00000	0.00000	0.00000	0.00000	Difference
1.4E-14	1.3E-14	7.9E-20	2.5E-15	1.0E-15	Difference squared
				3.1E-14	Sum of squared differences
46%	**43%**	**0%**	**8%**	**3%**	Uncertainty contribution
				100%	Sum of uncertainty contributions

Auxiliry parameters

Denotion	Value	Unit	
a	4.981E-08	-	Function of pure water density
b	8.185E-06	-	Function of pure water density
c	6.106E-05	-	Function of pure water density
d	0.9998599	-	Function of pure water density
pure water density	0.998206	kg/dm^3	
KIO3 solution density change	0.009105	$kg/dm^3/\%$	
KIO3 solution density correction	0.000259	kg/dm^3	
Kragten factor	10	-	

Uncertainty evaluation for SGW in 22.02.2008: Determination of $C_{Na2S2O3}$

$$C_{Na_2S_2O_3} = 6 \cdot C_{KIO_3} \cdot \Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3}} \cdot F_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3\_endp}} \cdot F_{I_2}$$

Input quantities				Uncertainty components of input quantities							
Denotion	Uncorr value	u_c	Unit	u	component	u	component	u	component	u	component
C_{KIO3}	0.0013	0.00000	mol/kg								
m_{KIO3}	2.9478	0.00028	g	0.00028	repeatability						
	2.9163		g								
	2.9531		g								
	2.9637		g								
	2.9475		g								
	2.9470		g								
$m_{Na2S2O3\_KIO3}$	9.5206		g								
	9.4149		g								
	9.5244		g								
	9.5574		g								
	9.5338		g								
	9.5591		g								
F_{m_KIO3}	1	0.00004	-	0.000029	rounding1	0.000029	rounding2	0.000115	linearity	0.000007	drift
$F_{m\_Na2S2O3\_KIO3}$	1	0.00001	-	0.000029	rounding1	0.000029	rounding2	0.000115	linearity	0.000023	drift
$F_{m\_KIO3\_endp}$	1	0.00103	-	0.001031	endpoint						
F_{I2}	1	0.00020	-	2.0E-04	volatility						

Input quantities					Uncertainty evaluation using the Kragten approach						
Denotion	Corr value	Unit	u_c	Relative	C_{KIO3}	$\Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}}$	F_{m_KIO3}	$F_{m\_Na2S2O3\_KIO3}$	$F_{m\_KIO3\_endp}$	F_{I2}	
C_{KIO3}	0.0013	mol/kg	0.000002	0.13%	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	
$\Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}}$	0.3095	-	0.00028	0.09%	0.3095	0.3095	0.3095	0.3095	0.3095	0.3095	
F_{m_KIO3}	1	-	0.00004	0.00%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_Na2S2O3\_KIO3}$	1	-	0.00001	0.00%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_KIO3\_endp}$	1	-	0.0010	0.10%	1.0000	1.0000	1.0000	1.0000	1.0001	1.0000	
F_{I2}	1	-	0.0002	0.02%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$C\_Na_2S_2O_3$	**0.002471**	**mol/kg**	**0.000005**	**0.19%**	0.00247	0.00247	0.00247	0.00247	0.00247	0.00247	Value
					3.3E-07	2.2E-07	1.0E-08	3.2E-09	2.5E-07	5.0E-08	Difference
					1.1E-13	4.9E-14	1.1E-16	1.0E-17	6.5E-14	2.5E-15	Difference squared
										2.2E-13	Sum of squared differences
					48%	**22%**	**0%**	**0%**	**29%**	**1%**	Uncertainty contribution
										100%	Sum of uncertainty contributions

Auxiliry parameters		
Denotion	Value	Unit
Number of titrations	6	
Kragten factor	10	-

Uncertainty evaluation for SGW in 22.08.2008: Determination of C_{O2_reag}

$$C_{\mathrm{O_2\_reag}} = \frac{1}{4} \cdot M_{\mathrm{O_2}} \cdot C_{\mathrm{Na_2S_2O_3}} \cdot \Gamma_{m_{\mathrm{reag}}}^{m_{\mathrm{Na_2S_2O_3\_reag}}} \cdot F_{m_{reag}} \cdot F_{m_{Na_2S_2O_3\_reag}} \cdot F_{m_{reag\_endp}} \cdot F_{I_2} - \frac{O_{2\_\mathrm{syringe}}}{m_{\mathrm{reag}}}$$

Input quantities				Uncertainty components of input quantities							
Denotion	Uncorr value	u_c	Unit	u	component	u	component	u	component	u	component
M_{O2}	31999	0.4500	mg/mol	0.15	O						
$C_{Na2S2O3}$	0.002471	0.000005	mol/kg								
$m_{Na2S2O3\_reag}$	0.9382	0.00327		0.00327	repeatability						
	0.9269		g								
	0.9648		g								
	0.8349		g								
	0.8876		g								
	0.9024		g								
m_{reag}	5.2590		g								
	5.2121		g								
	5.2899		g								
	5.2287		g								
	5.2016		g								
	5.2179		g								
$O_{2\_syringe}$	2.6893	0.27	µg	0.27	repeatability						
	1.6239		µg								
	2.9978		µg								
	1.2286		µg								
	2.0276		µg								
	2.0831		µg								
F_{m_reag}	1	0.000024	-	0.000029	rounding1	0.000029	rounding2	0.000115	linearity	0.0000126	drift
$F_{m\_Na2S2O3\_reag}$	1	0.000135	-	0.000029	rounding1	0.000029	rounding2	0.000115	linearity	0.0000022	drift
$F_{m\_reag\_endp}$	1	0.021592	-	0.0216	endpoint						
F_{I2}	1	0.00020	-	2.0E-04	volatility						

Input quantities					Uncertainty evaluation using the Kragten approach									
Denotion	**Corr value**	**Unit**	u_c	**Relative**	M_{O2}	$C_{Na2S2O3}$	$\Gamma^{m_{Na_2S_2O_{3\_reag}}}_{m_{reag}}$	$O_{2\_syringe}$	m_{reag}	F_{m_reag}	$F_{m\_Na2S2O3\_reag}$	$F_{m\_reag\_endp}$	F_{I2}	
M_{O2}	31999	mg/mol	0.45	0.00%	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	
$C_{Na2S2O3}$	0.0025	mol/kg	0.000005	0.19%	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	
$\Gamma^{m_{Na_2S_2O_{3\_reag}}}_{m_{reag}}$	0.1736	-	0.00327	1.88%	0.1736	0.1736	0.1740	0.1736	0.1736	0.1736	0.1736	0.1736	0.1736	
$O_{2\_syringe}$	2.1084	µg	0.27	12.7%	2.1084	2.1084	2.1084	2.1351	2.1084	2.1084	2.1084	2.1084	2.1084	
m_{reag}	5.2349	g	0.0000	0.00%	5.2349	5.2349	5.2349	5.2349	5.2349	5.2349	5.2349	5.2349	5.2349	
F_{m_reag}	1	-	0.000024	0.00%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_Na2S2O3\_reag}$	1	-	0.000135	0.01%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_reag\_endp}$	1	-	0.021592	2.16%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0022	1.0000	
F_{I2}	1	-	0.000200	0.02%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
C_{O2_reag}	**3.02914**	**mg/kg**	**0.11**	**3.7%**	3.0291	3.0298	3.0356	3.0240	3.0291	3.0291	3.0292	3.0366	3.0292	Value
					4.8E-06	6.6E-04	6.5E-03	-5.1E-03	0.0E+00	8.1E-06	4.6E-05	7.4E-03	6.9E-05	Difference
					2.3E-11	4.3E-07	4.2E-05	2.6E-05	0.0E+00	6.5E-11	2.1E-09	5.5E-05	4.7E-09	Difference squared
													1.2E-04	Sum of squared differences
					0%	**0%**	**34%**	**21%**	**0%**	**0%**	**0%**	**45%**	**0%**	Uncertainty contribution
													100%	Sum of uncertainty contributions

Auxiliry parameters		
Denotion	**Value**	**Unit**
Number of titrations	6	
Kragten factor	10	-

Uncertainty evaluation for SGW in 22.08.2008: Determination of C_{O2_s}

$$C_{O_2\_s} = \frac{1}{4} \cdot M_{O_2} \cdot C_{Na_2S_2O_3} \cdot \Gamma_{m_s}^{m_{Na_2S_2O_3\_s}} \cdot F_{m_s} \cdot F_{m_{Na_2S_2O_3\_s}} \cdot F_{m_{s\_endp}} \cdot F_{I_2} - C_{O_2\_reag} \cdot \Gamma_{m_s}^{m_{reag\_s}} - \frac{O_{2\_syringe}}{m_s}$$

Input quantities				Uncertainty components of input quantities							
Denotion	Uncorr value	u_c	Unit	u	component	u	component	u	component	u	component
M_{O2}	31999	0.45000	mg/mol	0.15	O						
$C_{Na2S2O3}$	0.0025	0.000005	mol/kg								
$m_{Na2S2O3\_s}$	4.3282	0.00056	g	0.00056	repeatability						
	4.3033		g								
	4.2946		g								
	4.2972		g								
	4.3057		g								
	4.3009		g								
m_s	9.2620		g								
	9.2634		g								
	9.2690		g								
	9.2390		g								
	9.2793		g								
	9.2602		g								
C_{O2_reag}	3.0291	0.11	mg/kg								
m_{reag_s}	0.5262	0.00128	g	0.00128	repeatability						
	0.5177		g								
	0.5191		g								
	0.5379		g								
	0.5171		g								
	0.4553		g								
$O_{2\_syringe}$	2.6893	0.26736	µg	0.27	repeatability						
	1.6239		µg								
	2.9978		µg								
	1.2286		µg								
	2.0276		µg								
	2.0831		µg								
F_{m_s}	1	0.00001	-	0.000029	rounding1	0.000029	rounding2	0.000115	linearity	0.000022	drift
$F_{m\_Na2S2O3\_s}$	1	0.00003	-	0.000029	rounding1	0.000029	rounding2	0.000115	linearity	0.000010	drift
$F_{m\_s\_endp}$	1	0.00228	-	0.00228	endpoint						
F_{I2}	1	0.00020	-	2.0E-04	volatility						

Input quantities					Uncertainty evaluation using the Kragten approach											
Denotion	Corr value	Unit	u_c	Relative	M_{O2}	$C_{Na2S2O3}$	$\Gamma^{m_{Na_2S_2O_3\_s}}_{m_s}$	C_{O2_reag}	$\Gamma^{m_{reag\_sample}}_{m_{sample}}$	$O_{2\_syringe}$	m_s	F_{m_s}	$F_{m\_Na2S2O3\_s}$	$F_{m\_s\_endp}$	F_{I2}	
M_{O2}	31999	mg/mol	0.450	0.00%	31999	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	31998.8	
$C_{Na2S2O3}$	0.0025	mol/kg	0.000	0.19%	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	
$\Gamma^{m_{Na_2S_2O_3\_s}}_{m_s}$	0.4648	-	0.001	0.12%	0.4648	0.4648	0.4648	0.4648	0.4648	0.4648	0.4648	0.4648	0.4648	0.4648	0.4648	
$C_{O2\ reag}$	3.029	mg/kg	0.111	3.67%	3.0291	3.0291	3.0291	3.0402	3.0291	3.0291	3.0291	3.0291	3.0291	3.0291	3.0291	
$\Gamma^{m_{reag\_s}}_{m_s}$	0.0553	g	0.0013	2.32%	0.0553	0.0553	0.0553	0.0553	0.0554	0.0553	0.0553	0.0553	0.0553	0.0553	0.0553	
$O_{2\_syringe}$	2.108	µg	0.267	12.68%	2.1084	2.1084	2.1084	2.1084	2.1084	2.1351	2.1084	2.1084	2.1084	2.1084	2.1084	
m_s	9.262	g	0.000	0.00%	9.2622	9.2622	9.2622	9.2622	9.2622	9.2622	9.2622	9.2622	9.2622	9.2622	9.2622	
F_{m_s}	1	-	0.000	0.00%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_Na2S2O3\_s}$	1	-	0.000	0.00%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_s\_endp}$	1	-	0.002	0.23%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0002	1.0000	
F_{I2}	1	-	0.000	0.02%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
C_{O2_s}	**8.79**	**mg/kg**	**0.042**	**0.48%**	8.7909	8.7927	8.7920	8.7903	8.7905	8.7880	8.7909	8.7909	8.7909	8.7930	8.7911	Value
C_{O2_s}	**8.78**	**mg/dm³**	**0.042**	**0.48%**	0.0000	1.8E-03	1.1E-03	-6.1E-04	-4E-04	-2.9E-03	0E+00	1.2E-05	2.6E-05	2.1E-03	1.8E-04	Difference
					0.0000	3.1E-06	1.2E-06	3.8E-07	1.5E-07	8.3E-06	0E+00	1.5E-10	6.8E-10	4.4E-06	3.4E-08	Difference squared
															1.8E-05	Sum of squared differences
					0%	**18%**	**7%**	**2%**	**1%**	**47%**	**0%**	**0%**	**0%**	**25%**	**0%**	Uncertainty contribution
															100%	Sum of uncertainty contributions

Auxiliry parameters

Denotion	Value	Unit	
Number of titrations	6		
a	5E-08	-	Function of pure water density
b	8.2E-06	-	Function of pure water density
c	6.1E-05	-	Function of pure water density
d	0.99986	-	Function of pure water density
temperature of water	20.0	°C	
density of pure water	0.9982	kg/dm³	
correction of air saturated water density	-3.2E-06	kg/dm³	
density of air saturated water	0.9982	kg/dm³	
Kragten factor	10	-	

APPENDIX 5

Uncertainty evaluation for FGW in 30.01.2012: Input quantities

Constants:		
$M(KIO_3)$=	214.00097	g/mol
$M(O_2)$=	31998.8	mg/mol
$M(Na_2S_2O_3)$=	158.108	g/mol
Date:		
30-Jan-2012		
Operator:		
Irja Helm		
p_Vaisala=	104289	Pa
t_Chub=	24.90	°C
C_{O2}Ref=	8.542	[mg/dm^3]
***U*(C_{O2}Ref) =**	0.065	[mg/dm^3]
Δ=	-0.004	[mg/dm^3]

Preparation of the KIO_3 standard solution

7-Oct-11

Primary solution KIO_3 I

m(flask)=	24.27969 g		
m(flask+KIO_3_s)=	25.67851 g	⇨	m(solution) 38.74661 g
m(KIO_3_s)=	1.39882 g		c(solution) 36101.827 mg/kg
m(flask+KIO_3I)=	63.02630 g		

9-Jan-12

Secondary solution KIO_3 II

m(flask)=	27.42392 g		
m(flask+KIO_3I)=	31.06630 g	⇨	m(solution) 37.06656 g
m(KIO_3 I)=	3.64237 g		c(solution) 3547.5731 mg/kg
m(flask+KIO_3II)=	64.49048 g		

27-Jan-12

Working solution KIO_3 III

m(flask)=	97.7426 g	⇨	
m(flask+KIO3II)=	102.8880 g		m(solution) 96.59347 g
m(KIO3 II)=	5.14533 g		c(solution) 188.97185 mg/kg
m(flask+KIO3III)=	194.3361 g		

Determination of the $Na_2S_2O_3$ solution concentration

Nr	m(tare) (g)	m(tare + KIO_3) (g)	m(KIO_3) (g)	m(titr syr before) (g)	m(titr syr after) (g)	m(titrant) (g)
1	20.60535	25.47930	4.87395	32.97503	15.81398	17.16105
2	21.62533	26.22042	4.59509	32.56234	16.39622	16.16612
3	20.12579	24.99128	4.86549	32.73514	15.61546	17.11968
4	21.26223	26.08841	4.82618	32.36815	15.39320	16.97495
5	20.49135	25.35827	4.86692	32.77649	15.64416	17.13233
6	20.26203	25.14634	4.88431	32.78205	15.59120	17.19085
7	20.50111	25.32389	4.82278	33.84083	16.87373	16.96710
arithmetic mean			4.81925			16.95887

Determination of the O_2 concentration in sample

ρ= 0.997074411 "+" 7.73831E-06 "=" 0.997082149 g/cm^3

Nr	V(s.bottle) (cm^3)	V(sample) (cm^3)	m(sample) (g)	m(titr syr before) (g)	m(titr syr after) (g)	m(titrant) (g)
1	11.82361	11.41237	11.37907	32.71434	24.52099	8.19335
2	11.77924	11.36801	11.33484	32.56797	24.42122	8.14675
3	11.89705	11.48581	11.45230	32.66569	24.42856	8.23713
4	11.87858	11.46735	11.43389	32.95339	24.73213	8.22126
6	11.88738	11.47615	11.44266	32.45531	24.22320	8.23211
7	11.84125	11.43002	11.39667	32.84362	24.64559	8.19803
8	11.73808	11.32684	11.29379	32.81941	24.68239	8.13702
arithmetic mean			11.39046	32.71710	24.52201	8.19509

Input quantities:

rep_low	0.000043	g
rep_high	0.000057	g
rounding_low	0.0000029	g
rounding_high	0.0000289	g
drift	0.00000080	
calibration	0.00000042	
u(evaporation H_2O)	0.00147537	g
u(warming effect)	0.00045611	g
V($MnSO_4$_H_2O)	0.205981334	cm^3
s(V_H_2O_1)	0.0009898	cm^3
V(KOHKI_H_2O)	0.205252695	cm^3
s(V_H_2O_2)	0.0004596	cm^3
Mass of the drop	0.011	g
n_I_2vol_t	0.0000325	mmol
st.dev.n_I_2vol_t	0.0000074	mmol
u(± titration time)	0.0000081233	mmol
cal 5°C	0.000032	
cal 25°C	0.000338	
n_I_2vol_s	0.0000116	mmol
st.dev.n_I_2vol_s	0.0000014	mmol
Int_{O2}	0.00256	mg/kg
CF_{O2}	0.094014806	mg/kg
u(CF_{O2})	0.006833671	mg/kg

Uncertainty evaluation for FGW in 30.01.2012: Determination of C_{KIO3_III}

$$C_{KIO_3III}\left[\frac{mol}{kg}\right]=\frac{m_{KIO_3\_s}[g]\cdot 1000\left[\frac{g}{kg}\right]\cdot 1000\left[\frac{mg}{g}\right]\cdot m_{KIO_3\_I\_transf}[g]\cdot m_{KIO_3\_II\_transf}[g]\cdot P_{KIO_3}[-]}{M_{KIO_3}\left[\frac{mg}{mol}\right]\cdot m_{KIO_3\_I}[g]\cdot m_{KIO_3\_II}[g]\cdot m_{KIO_3\_III}[g]}$$

Input quantities				Uncertainty components of input quantities													
Denotion	Uncorr value	u_c	Unit	u	component	u	component	u	component	u	component	u	component	u	component	u	component
$m(KIO_3)s$	1.399	0.000061	g	0.000043	repeatability1	0.000003	rounding1	0.000043	repeatability2	0.000003	rounding2	0.00000112	drift	0.00000058	calibration		
P_KIO_3	1.000	0.000577	-	0.000577	purity												
M_KIO_3	214000.97	0.453018	mg/mol	0.05	K	0.015	I	0.15	O								
$m(KIO_3I\_transf)$	3.642	0.001477	g	0.000043	repeatability1	0.000003	rounding1	0.000043	repeatability2	0.000003	rounding2	0.00000291	drift	0.00000152	calibration	0.00148	evaporation
$m(KIO_3II\_transf)$	5.145	0.001478	g	0.000057	repeatability1	0.000029	rounding1	0.000057	repeatability2	0.000029	rounding2	0.00000412	drift	0.00000214	calibration	0.00148	evaporation
$m(KIO_3I)$	38.747	0.000070	g	0.000043	repeatability1	0.000003	rounding1	0.000043	repeatability2	0.000003	rounding2	0.00003100	drift	0.00001614	calibration		
$m(KIO_3II)$	37.067	0.000096	g	0.000057	repeatability1	0.000029	rounding1	0.000057	repeatability2	0.000029	rounding2	0.00002965	drift	0.00001544	calibration		
$m(KIO_3III)$	96.593	0.000125	g	0.000057	repeatability1	0.000029	rounding1	0.000057	repeatability2	0.000029	rounding2	0.00007727	drift	0.00004025	calibration		

Input quantities					Uncertainty evaluation using the Kragten approach								
Denotion	Corr value	Unit	u_c	Relative	$m(KIO_3)s$	P_KIO_3	M_KIO_3	$m(KIO_3I\_transf)$	$m(KIO_3II\_transf)$	$m(KIO_3I)$	$m(KIO_3II)$	$m(KIO_3III)$	
$m(KIO_3)s$	1.3988	g	0.00006	0.0044%	1.399	1.3988	1.3988	1.399	1.399	1.399	1.399	1.399	
P_KIO_3	1.00000	-	0.00058	0.0577%	1.00000	1.00006	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	
M_KIO_3	214000.97	mg/mol	0.45302	0.0002%	214000.97	214000.97	214001.02	214000.97	214000.97	214000.97	214000.97	214000.97	
$m(KIO_3I\_transf)$	3.6424	g	0.00148	0.0405%	3.642	3.6424	3.6424	3.643	3.642	3.642	3.642	3.642	
$m(KIO_3II\_transf)$	5.1453	g	0.00148	0.0287%	5.145	5.1453	5.1453	5.145	5.145	5.145	5.145	5.145	
$m(KIO_3I)$	38.7466	g	0.00007	0.0002%	38.747	38.7466	38.7466	38.747	38.747	38.747	38.747	38.747	
$m(KIO_3II)$	37.0666	g	0.00010	0.0003%	37.067	37.0666	37.0666	37.067	37.067	37.067	37.067	37.067	
$m(KIO_3III)$	96.5935	g	0.00013	0.0001%	96.593	96.5935	96.5935	96.593	96.593	96.593	96.593	96.593	
C_KIO_3	**0.0008830**		**0.0000007**	**0.076%**	**0.0008830**	**0.0008831**	**0.0008830**	**0.0008831**	**0.0008831**	**0.0008830**	**0.0008830**	**0.0008830**	Value
					0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	Difference
					1.5E-17	2.6E-15	3.5E-20	1.3E-15	6.4E-16	2.6E-20	5.2E-20	1.3E-20	Difference squared
												4.5E-15	Sum of squared differences
					0%	**57%**	**0%**	**28%**	**14%**	**0%**	**0%**	**0%**	Uncertainty contribution
												4.5E-15	Sum of uncertainty contributions

Auxiliry parameters		
Denotion	Value	Unit
Number of titrations	7	-
Kragten factor	10	-

Uncertainty evaluation for FGW in 30.01.2012: Determination of $C_{Na2S2O3}$

$$C_{Na_2S_2O_3}[\frac{mol}{kg}] = 6 \cdot C_{KIO_3}[\frac{mol}{kg}] \cdot \Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3}} \cdot F_{m_{Na_2S_2O_3\_KIO_3}} \cdot F_{m_{KIO_3\_endp}} - \frac{2 \cdot n_{I_2\_vol\_t}[mmol]}{m_{Na_2S_2O_3\_KIO_3}[g]}$$

Input quantities					Uncertainty components of input quantities									
Denotion	**Uncorr value**	**correction**	u_c	**Unit**	***u***	**component**	***u***	**component**	***u***	**component**	***u***	**component**	***u***	**component**
c_{KIO3}	0.00088304		0.0000006737	**mol/kg**										
m_{KIO3}	4.87395000		0.0000400270	**g**	0.00004	**repeatability**								
	4.59509000			**g**										
	4.86549000			**g**										
	4.82618000			**g**										
	4.86692000			**g**										
	4.88431000			**g**										
	4.82278000			**g**										
$m_{Na2S2O3\_KIO3}$	17.16105000			**g**										
	16.16612000			**g**										
	17.11968000			**g**										
	16.97495000			**g**										
	17.13233000			**g**										
	17.19085000			**g**										
	16.96710000			**g**										
$F_{m\_Na2S2O3\_KIO3}$	1.00000000		0.0000269024	-	0.000003	**rounding1**	0.000003	**rounding2**	0.000007066	**calibration**	0.0000071	**drift**	0.000456107	**warming efect**
F_{m_KIO3}	1.00000000		0.0000635368	-	0.000003	**rounding1**	0.000003	**rounding2**	0.000002008	**calibration**	0.0000039	**drift**	0.000306142	**evaporation**
$F_{m\_KIO3\_endp}$	1.00000000		0.0001787318	-	0.000179	**endpoint**								
$n_{I2\_vol\_t}$	0.00003249		0.0000087238	**mmol**	0.0000074	**eksp.st.h.**	0.0000047	±15 sek						

Input quantities					Uncertainty evaluation using the Kragten approach						
Denotion	**Corr value**	**Unit**	u_c	**Relative**	**CKIO3**	$\Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}}$	F_{m_KIO3}	$F_{m\_Na2S2O3\_KIO3}$	$F_{m\_KIO3\_endp}$	$n_{I2\_vol\_t}$	
CKIO3	0.0009	**mol/kg**	0.000001	0.08%	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	
$\Gamma^{m_{KIO_3}}_{m_{Na_2S_2O_3\_KIO_3}}$	0.28417350	-	0.00004003	0.01%	0.2842	0.2842	0.2842	0.2842	0.2842	0.2842	
$F_{m\_Na2S2O3\_KIO3}$	1.00000	-	0.00003	0.00%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
F_{m_KIO3}	1	-	0.00006	0.01%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$F_{m\_KIO3\_endp}$	1	-	0.0002	0.02%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	
$n_{I2\_vol\_t}$	0.000032	**mmol**	0.0000	26.85%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
C_Na2S2O3	**0.0015018**	**mol/kg**	**0.0000016**	**0.11%**	0.00150	0.00150	0.00150	0.00150	0.00150	0.00150	Value
					1.1E-07	2.1E-08	4.1E-09	9.6E-09	2.7E-08	-1.0E-07	Difference
					1.3E-14	4.5E-16	1.6E-17	9.2E-17	7.2E-16	1.1E-14	Difference squared
										2.5E-14	Sum of squared differences
					53%	**2%**	**0%**	**0%**	**3%**	**42%**	Uncertainty contribution
										100%	Sum of uncertainty contributions

Auxiliry parameters		
Denotion	**Value**	**Unit**
Number of titrations	7	
Kragten factor	10	-

Uncertainty evaluation for FGW in 30.01.2012: Determination of C_{O2_s}

$$C_{O_2\_s}\left[\frac{mg}{dm^3}\right] = \rho[\frac{kg}{dm^3}]\cdot\left(M_{O_2}[\frac{mg}{mol}]\cdot\frac{1}{4}\cdot\left(C_{Na_2S_2O_3}[\frac{mol}{kg}]\cdot\Gamma_{m_s}^{m_{Na_2S_2O_3\_s}} + \frac{2\cdot n_{I_2\_vol\_s}[mmol]}{\overline{m_s[g]}}\right)\cdot F_{m_s}\cdot F_{m_{Na_2S_2O_3\_s}}\cdot F_{m_{s\_endp}} - Int_{O_2}[\frac{mg}{kg}] - CF_{O_2}\left[\frac{mg}{kg}\right]\cdot\frac{P[Pa]}{101325[Pa]}\right)$$

Input quantities				Uncertainty components of input quantities															
Denotion	Uncorr value	u_c	Unit	u	component	u	component	u	component	u	component	u	component	u	component	u	component	u	component
M_{O2}	31998.80	0.45000	mg/mol	0.15	0														
$C_{Na2S2O3}$	0.0015	0.000002	mol/kg																
$m_{Na2S2O3\_s}$	8.1934	0.00023	g	0.00023	repeatability														
	8.1468		g																
	8.2371		g																
	8.2213		g																
	8.2321		g																
	8.1980		g																
	8.1370		g																
m_s	11.3791	0.00003	g																
	11.3348		g																
	11.4523		g																
	11.4339		g																
	11.4427		g																
	11.3967		g																
	11.2938		g																
CF_{O2}	0.09401	0.006833671	mg/kg	0.00683	eksp.st.dev														
P	104289	3.5	Pa	3.50	Certificate														
F_{m_s}	1	0.000150160	-	0.00034	cal25°C	0.000032	cal5°C	0.00000025	rounding1	0.00000025	rounding2	0.00000080	drift	0.0000047	calibration	0.0015	cal MnSO4	0.00071	cal KOHKI
$F_{m\_Na2S2O3\_s}$	1	0.000055666	-	0.000003	rounding1	0.0000029	rounding2	0.0000066	drift	0.0000034	calibration	0.000456	warming efect						
$F_{m\_s\_endp}$	1	0.000369866	-	0.00037	endpoint														
$n_{I2\_vol\_s}$	0.000012	0.000001412	mmol	0.00000	st.dev														
Int_{O2}	0	0.002563435	mg/kg	0.002563															

Input quantities					Uncertainty evaluation using the Kragten approach										
Denotion	Corr value	Unit	u_c	Relative	M_{O2}	$C_{Na2S2O3}$	$\Gamma_{m_s}^{m_{Na_2S_2O_{3\_s}}}$	CF_{O2}	P	F_{m_s}	$F_{m\_Na2S2O3\_s}$	$F_{m\_s\_endp}$	$n_{I2\_vol\_s}$	Int_{O2}	
M_{O2}	31999	mg/mol	0.450	0.00%	31999	31999	31999	31999	31999	31999	31999	31999	31999	31999	
$C_{Na2S2O3}$	0.0015	mol/kg	0.000	0.11%	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0	
$\Gamma_{m_s}^{m_{Na_2S_2O_{3\_s}}}$	0.719471	-	0.0002266	0.03%	0.7195	0.7195	0.7195	0.7195	0.7195	0.7195	0.7195	0.7195	0.7195	0.7	
CF_{O2}	0.0940	mg/kg	0.0068	7.27%	0.0940	0.0940	0.0940	0.0947	0.0940	0.0940	0.0940	0.0940	0.0940	0.1	
P	104289	Pa	3.500	0.00%	104289	104289	104289	104289	104289	104289	104289	104289	104289	104289	
F_{m_s}	1	-	0.000	0.02%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0	
$F_{m\_Na2S2O3\_s}$	1	-	0.000	0.01%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0	
$F_{m\_s\_endp}$	1	-	0.000	0.04%	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0	
$n_{I2\_vol\_s}$	0.000012	mmol	0.000	12.23%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0	
Int_{O2}	0	mg/kg	0.003		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0	
C_{O2_s}	**8.563**	**mg/kg**	**0.013**	**0.15%**	8.5631	8.5640	8.5634	8.5624	8.5631	8.5632	8.5631	8.5634	8.5633	8.5634	Value
C_{O2_s}	**8.538**	**mg/dm^3**	**0.013**	**0.15%**	0.0000	0.0009	0.0003	-0.0007	0.0000	0.0001	0.0000	0.0003	0.0002	0.0003	Difference
					0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	Difference squared
														1.6E-06	Sum of squared differences
					0.0%	**51.1%**	**4.6%**	**30.4%**	**0.0%**	**1.0%**	**0.1%**	**6.3%**	**2.4%**	**4.0%**	Uncertainty contribution
														100%	Sum of uncertainty contributions

Auxiliry parameters

Denotion	Value	Unit	
Number of titrations	7		
a	4.98E-08	-	Function of pure water density
b	8.18E-06	-	Function of pure water density
c	6.11E-05	-	Function of pure water density
d	0.99986	-	Function of pure water density
temperature of water	24.9	°C	
density of pure water	0.9971	kg/dm^3	
corr of air saturated water density	-2.9E-06	kg/dm^3	
density of air saturated water	0.9971	kg/dm^3	
Kragten factor	10	-	

PUBLICATIONS

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Main scientific publications

1. Jalukse, L.; Helm, I.; Saks, O.; Leito, I.. On the accuracy of micro Winkler titration procedures: a case study. *Accreditation and Quality Assurance*, **2008**, 13 (10), 575–579.
2. Helm, I; Jalukse, L; Vilbaste, M.; Leito, I. Micro-Winkler titration method for dissolved oxygen concentration measurement. *Analytica Chimica Acta.* **2009**, 648 (2), 167–173.
3. Helm I., Jalukse L., Leito I. Measurement Uncertainty Estimation in Amperometric Sensors: A Tutorial Review. *Sensors*. **2010**, 10 (5), 4430–4455.
4. I. Helm, L. Jalukse, I. Leito, A new primary method for determination of dissolved oxygen: gravimetric Winkler method. *Analytica Chimica Acta*, **2012**, 741, 21–31.

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Tähtsamad teaduspublikatsioonid

1. Jalukse, L.; Helm, I.; Saks, O.; Leito, I.. On the accuracy of micro Winkler titration procedures: a case study. *Accreditation and Quality Assurance*, **2008**, 13 (10), 575–579.
2. Helm, I; Jalukse, L; Vilbaste, M.; Leito, I. Micro-Winkler titration method for dissolved oxygen concentration measurement. *Analytica Chimica Acta.* **2009**, 648 (2), 167–173.
3. Helm I., Jalukse L., Leito I. Measurement Uncertainty Estimation in Amperometric Sensors: A Tutorial Review. *Sensors*. **2010**, 10 (5), 4430–4455.
4. I. Helm, L. Jalukse, I. Leito, A new primary method for determination of dissolved oxygen: gravimetric Winkler method. *Analytica Chimica Acta*, **2012**, 741, 21–31.

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